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The Dielectric Properties of Mixtures of Organic Compounds and Perfluoropropane

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THE DIELECTRIC PROPERTIES OF MIXTURES OF ORGANIC COMPOUNDS AND PERFLUOROPROPANE

BY

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This thesis is approved as a creditable, independent investigation by a candidate for the degree, Master of Science, and acceptable as meeting the thesis requirements for this degree; but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Advisor

Head of the Major Department

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INTRODUCTION

The exact chemical changes taking place when gas molecules are exposed to electrical stress are not known. Of the many gases which might be studied, perfluoropropane was selected because of its interesting characteristics as a gas of high dielectric strength (29).

Many factors influence the breakdown process. It appears that the details of molecular structure are very important in determining the breakdown strength. As yet, no definite relation between dielectric properties and the molecular structure of a gas has been found. The effect of corona on the gas structure is also still not understood.

The processes taking place under electrical stress might be studied in several ways. The effects caused by breakdown and corona conditions may well lead to distinctive products which could cast some light on the process by which they were formed. However, if the breakdown and corona conditions lead to bond breaking or ion formation which in turn participates extensively in recombination or disproportionation type processes, the final products may be extremely few in number compared to the multitude of pathways by which they might have been formed. In order to understand these various pathways, the study of the final products formed would not be very fruitful. Other methods would be needed to assess the nature and quantity of the metastable intermediates formed.

In this study, an attempt was made to understand the type and amounts of metastable intermediates formed when perfluoropropane was placed under electrical stress by adding small amounts of organic

compounds such as thiophene, isopropyl mercaptan, ethyl methyl sulfide, dimethyl disulfide, carbon disulfide, and nitrobenzene. The sulfur compounds were chosen because fluorine was reported to react with thiophene to form sulfur hexafluoride (36). It was thought that if fluorine were formed from perfluorocarbons in the corona, it might be advantageous to remove this metastable species. Nitrobenzene was used because of its known free radical inhibitor characteristic in polymerization reactions. The hope was that these additive compounds might be effective in reducing corona or inhibiting breakdown by removing the metastable intermediates formed in the gas by the electrical stress. It was also hoped that the study of the decomposition products and the nature of effectiveness of the additives might provide an insight into the relationship of chemical structure and dielectric strength.

LITERATURE REVIEW

A theory of gaseous electrical insulation was proposed by Townsend (47) in 1901. This theory dealt with the nonself-maintained discharges which occurred when a potential was applied to gases. The current observed at the various applied voltages was ascribed to varying amounts of ions and electrons produced by several different means. At low voltages, the ions and electrons were considered to be produced primarily by natural radiative energy. At higher voltages the increase in current was explained by the dissociation of neutral molecules by bombardment with these radiatively produced electrons which were accelerated to a sufficiently high energy by the imposed field. As the field increased, the electrons produced by collision in turn produced other electrons thus initiating a chain reaction. The rate of ions produced by this process was experimentally determined and was expressed by an equation $J=J_o e^{\alpha d}$, where J is the electronic current, d is the distance between two uniform field electrodes and α is known as Townsend's coefficient. This quantity depends upon the electric field for a given gas at a given pressure. An insulating gas, therefore, has a very low conductivity as a result of its tendency to form few electrons, positive ions, or negative ions. In general, the Townsend coefficient is small.

Cragg and co-workers (11, 12) proposed that the mechanism of the negative ion formation in the electron bombardment of polyatomic compounds to be either class 1: $xy+e \longrightarrow x+y^-$ or class 2: $xy+e \longrightarrow x^++y^-+e$. As in Townsend's considerations, the primary process in all gaseous

breakdowns was considered to be the multiplication of electrons in a gas by cumulative ionization caused by electron impact. This multiplication of electrons was pictured as advancing in the direction of the electric field. Loeb (28) in a more detailed consideration of the mechanism discussed secondary processes acting in conjunction with the above primary process. The relatively frequently encountered secondary processes were divided into two categories. The first of these was the secondary processes at the cathode. These processes consisted of (a) liberation of secondary electrons by positive ion bombardment, (b) liberation of secondary electrons by photoelectric processes and (c) liberation of secondary electrons by metastable species. The second category included the secondary processes in the gas. These consisted of (a) ionization of the gas by metastable species, and (b) the photoelectric ionization of the gas by photons.

Fairly earnest work was started in studying gases as practical dielectrics around 1936. Air, nitrogen, hydrogen, hydrocarbon gases, freon, and freon-air mixtures have been studied (26, 34, 33, 15) for high voltage breakdown characteristics at atmospheric pressure and higher pressures. In general a gas at higher pressures broke down at higher voltages.

The fluorocarbon gases which became generally available after World War II were found to have dielectric characteristics superior to those of other halogenated gaseous compounds (6, 8, 38, 41, 22). The compounds investigated by Berberich and co-workers (6) are listed in Table I. It was noted with interest that perfluorophenanthrane, $C_{14}F_{24}$,

TABLE I. PHYSICAL PROPERTIES AND BREAKDOWN VOLTAGE OF VARIOUS GASES

Name of Compound	Molecular Formula	Molecular Weight	Liquid Density at 20°C.	Refractive Index at 20°C.	Boiling Point °C.	Vapor Pressure at 25°C. MMHG	Relative 60 Cycle Breakdown at 30 CMHG
Nitrogen	N_2	28	0.808 at -196°C.		-196	Gaseous	1
Perfluoromethane	CF_4	88	1.96 at -184°C. gas 0.60		-128	Gaseous	1.25
Perfluoropropane	C_3F_8	188	1.45 gas 0.61		- 38	Gaseous	2
Sulfur Hexafluoride	SF_6	146	1.91		- 63.8	Gaseous	2.5
Perfluoroheptane	C_7F_{16}	388	1.733	1.2618	82	110	5.5
Perfluor-Triethylamine	NC_6F_{15}	371	1.749	1.262 at 25°C.	71	130	6.
Perfluoromethyl-Cyclohexane	C_7F_{14}	350	1.7994	1.2815	76	110	6.
Perfluorotoluene	C_7F_8	236	1.660	1.3664	102	23	7.
Perfluorodibutyl-Ether	$C_8F_{18}O$	454	1.717 at 25°C.	1.26	100	33	7.5
Perfluorotri-N-Butylamine	$NC_{12}F_{27}$	671	1.88	1.29 at 25°C.	178	2.7	8.
Perfluorodimethyl Cyclohexane	C_8F_{16}	400	1.8503	1.2896	101	40	8.5
Perfluorophenanthrane	$C_{14}F_{24}$	624	2.019	1.3315	205	---	10.

had four times the breakdown value of sulfur hexafluoride, and ten times that of nitrogen. Perfluoromethylcyclohexane had a 60 cycle breakdown value under uniform field conditions and at one atmosphere pressure equal to that of oil tested in the same cell. Berberich and his group at Westinghouse (7) as well as Camilli and co-workers at General Electric (8, 9) have reported that perfluorocarbon vapors of straight chain and cyclic compounds when mixed with nitrogen showed suprisingly high dielectric breakdown values. Since the breakdown values of mixtures with nitrogen were greater than for the pure vapor at the same pressure, the practical implication was that less perfluorocarbon is required for a given dielectric strength by use of mixtures. The Westinghouse workers (7) and Wilson (51) also demonstrated that the dielectric strength of the fluorocarbons increased with increasing molecular weight or pressure (7, 51). Further work by Berberich showed that the breakdown strength of the straight chain compounds through perfluoropentane, C_5F_{12} (7) is approximately linearly related to the density of the vapor, and that the straight chain perfluorocarbons such as perfluoroheptane, C_7F_{16}, is not markedly different from that of the cyclic compound perfluorocycloheptane, C_7F_{14}. However, an outstanding exception was perfluorotoluene, C_7F_8 (7), which possesses a conjugated system of double bonds in the six member ring. It was not clear whether this lowering of breakdown strength was due to the considerably less fluorine in perfluorotoluene than in its saturated counterpart perfluorocycloheptane or to the resonating system of double bonds and the associated higher electronic polarizability which would facilitate the absorption of the

energy from free electrons in the early stages of the breakdown process. The perfluoroether, $(C_4F_9)_2O$, and the perfluoroamines, NC_6F_{15} and $NC_{12}F_{27}$, as well as perfluoroheptane all behaved similarly. The presence of the oxygen atom in the ether compound and the nitrogen in the amino compounds did not alter the breakdown behavior.

The unusually high dielectric strengths observed for fluorocarbon gases have been attributed by many workers (9, 23, 21, 27) to the electronegative character of fluorine. Especially detailed discussions can be found in books by Llewellyn-Jones (27) and Field and Franklin (21) both published in 1957. The explanations offered for the role of fluorine in the fluorocarbons can be summarized as follows. The covalently bonded fluorine, being strongly electronegative, is pictured as an effective electron trap in the early stages of the gaseous breakdown process and thereby increases the voltage at which final breakdown takes place. The initiation of breakdown processes for ordinary gases in a d-c field for an extremely divergent field such as a point to plane electrode system with the point positively charged is explained by considering that the electrons are attracted to the point from the weaker parts of the field, thus leaving a positive ion space charge which grows outward into a streamer with a concentrated electric field at its tip. These streamers form few branches because most of the electrons join the advancing streamer at its tip. When the point is negative, streamers also form. However, in this case, the positive space charge originates as a diffuse entity on the larger electrode and extends toward the negatively charged point electrode. This means that

the electrons leaving the point electrode are spread out into numerous weak branches scattered in all directions toward the diffuse positive space charge. It is because of this difference in electron concentration in streamer formation that a lower breakdown voltage is observed for the positive point electrode rather than for the case when the charges are reversed. The increase in the breakdown strength of gases containing electronegative atoms is explained by the great affinity of electronegative atoms for electrons. These electronegative atoms capture many free electrons before they can reach ionizing velocities. Thus streamer formation is inhibited. The slow negative ions formed through electron capture also reduce the positive space charge in the streamer, thus making necessary a higher voltage before the streamer can cross the gap. In common with other gases, electronegative gases may also extract energy from electrons without actual capture through inelastic collision. Inelastic collisions are more probable when large molecules are present. Such collisions are considered to be important because many of the perfluorocarbon vapors investigated are large molecules.

The breakdown voltages are determined not only by the nature of the gas but are also extremely sensitive to electrode configurations. Liao et al. (26) found that the sphere gap possessed a higher breakdown voltage value than in the coaxial cylinder gap under the same testing condition. Both were better than point to sphere or point to plane gap. Manning (29) found that the breakdown strength for perfluoropropane was less than that for sulfur hexafluoride using sphere to grounded plane

electrodes but that the reverse was true when square rod to grounded plane electrodes were used.

Cotton lint and dust have been shown to increase corona (9). The effect was most pronounced when the gas contained moisture. This was thought to be due to the probable increase in dielectric constant and conductivity caused by the dust absorbing the moisture. These workers also showed that the surface irregularities caused a lower breakdown value which rose on continued sparking due to removal of the irregularities.

At the dielectric breakdown potential, arcing between the electrodes occurs. It was noticed that except in the case of perfluoromethane, this arcing in fluorocarbons resulted in the formation of a thin layer of black material, probably carbon, on the surfaces of the electrodes and the glass flask, and that a pressure rise of about 1% of the total pressure occurred (51). This latter observation seemed to indicate that low molecular weight fluorocarbons formed to a slight extent during arcing. Simons and co-workers (45) on studying the reaction of perfluoromethane in a carbon arc found that half of the product was perfluoropropane and the remainder consisted of higher boiling fractions with no unsaturated compounds detectable. Carbonyl fluoride, COF_2 was also collected. This disagrees with the results of another investigator (43) who found that perfluoroethane and perfluoroethylene were the products of perfluoromethane when exposed to an arc between two carbon electrodes. In general, there is only a limited amount of information on chemical changes of perfluorocarbons on being exposed to arcs.

Pyrolysis or thermal decomposition studies are interesting because of the necessity of separating the thermal effects and the electrical effects of discharge on fluorocarbon gases. Steunenberg and Cady (46) studied the decomposition of perfluoroethylene, C_2F_4, perfluoroethane, C_2F_6, perfluoropropane, C_3F_8, perfluorobutane, C_4F_{10}, perfluoropentane, C_5F_{12} and cyclic perfluoropentane, C_5F_{10}, on platinum wire at 1000-1450°C. They mentioned the possibility of the pyrolysis being catalyzed by the platinum. The products found on pyrolysis of unsaturated compounds such as perfluoropropene, C_3F_6, carried out in glass at temperatures higher than 1000°C were perfluoromethane, CF_4, perfluoroethane, C_2F_6, CO and SiF_4. Perfluoropropane at temperatures above 1000°C was found to produce perfluoroethane, perfluoropropene, perfluorobutene and a perfluorocarbon polymer, $(-CF_2-)$. In the pyrolysis of perfluoropentane (42) on platinum at 850°C no reaction was observed; there was a slow reaction at 900°C; and at higher temperatures perfluoromethane, perfluoroethane, perfluoropropene and perfluoropropane were the products of this pyrolysis. Farlow (20) studied the pyrolysis of fluorocarbons of three carbons or more. The gas after exposure to a carbon arc was quenched to 400°C. The products were found to be perfluoromethane, perfluoroethylene, perfluoroethane and perfluoropropene. It is observed that the decomposition products formed from the platinum wire pyrolysis and the arc pyrolysis were similar.

Atkinson studied the pyrolysis of perfluoroethylene under milder conditions. In the mercury sensitized photochemical reaction of perfluoroethylene, hexafluorocyclopropane and polymer were formed (1).

In the thermal decomposition of perfluoroethylene at temperatures below 550°C, fluorine was formed, while at 600°C-700°C, the products were perfluoropropene, perfluorobutene-1 and perfluorobutene-2 (3). In a later paper (2) the reaction sequences for the products formed were postulated as follows:

The reaction producing perfluoropropene:

$$2CF_2 = CF_2 \longrightarrow (CF_2)_4$$

$$(CF_2)_4 \longrightarrow 2CF_2 = CF_2$$

$$(CF_2)_4 \longrightarrow CF_3CF = CF_2 + :CF_2$$

$$:CF_2 + CF_2 = CF_2 \longrightarrow CF_3 - CF = CF_2$$

The reaction producing perfluoroisobutene:

$$CF_3CF = CF_2 \longrightarrow CF_2 = CF_2 + :CF_2$$

$$:CF_2 + CF_3CF = CF_2 \longrightarrow (CF_3)_2C = CF_2$$

$$CF_2 = CF_2 + CF_3CF = CF_2 \longrightarrow (CF_3)_2C = CF_2 + :CF_2$$

$$2CF_3CF = CF_2 \longrightarrow CF_2 = CF_2 + (CF_3)_2C = CF_2$$

The disproportionation of perfluorobutene producing perfluoroethane:

$$(CF_3)_2C = CF_2 \longrightarrow {}^{\bullet}CF_3 + CF_3CF = CF^{\bullet}$$

$${}^{\bullet}CF_3 + (CF_3)_2C = CF_2 \longrightarrow CF_3 - CF_3 + CF_3CF = CF^{\bullet}$$

$$CF_3(CF = CF)^{\bullet}_m + CF_3(CF = CF)^{\bullet}_n \longrightarrow CF_3(CF = CF)^{\bullet}_{m+n} + {}^{\bullet}CF_3$$

This showed that if the pyrolysis proceeded by a free radical mechanism, even at the relatively low temperatures employed, it was definitely not the same as in the photochemical reaction.

Perfluoromethane, perfluoroethylene and perfluoropentane were investigated in the glow discharge. Weisz (49) found that the decomposition products of perfluoromethane in the glow discharge process reacted

with glass to give CO_2, CO, O_2 and SiF_4. Perfluoroethylene, on the other hand, was polymerized to a liquid polymer during the glow discharge. In the case of perfluoropentane (50) no detectable pyrolysis occurred at 840°C, slow pyrolysis took place at 900°C, and faster pyrolysis at higher temperatures. Perfluoromethane, perfluoroethane, perfluoropropane, perfluorobutene and perfluoropropene were the products. As in the arcing phenomena, extensive chemical work has not been carried out on the products formed on exposing perfluorocarbons to glow discharges.

Mass spectrometer studies are of interest since the metastable ions formed by electron bombardment in the instrument might be very similar in nature to the action of electrons in the corona. Mohler and co-workers (16, 30, 17, 31, 32) have extensively studied various perfluorocarbons in order to characterize these compounds for analytical determinations by use of the mass spectrometer and incidentally to determine the isotope abundance ratio for fluorine. Some of the main fluorocarbons which have been investigated in connection with this study (30) are listed in Table II.

TABLE II. COMPOUNDS STUDIED IN MASS SPECTROMETER

Normal Perfluoroparaffines	Perfluorocyclic	Perfluoro-olefins
CF_4	C_4F_8	C_2F_4
C_2F_6	C_5F_{10}	C_3F_6
C_3F_8	C_6F_{12}	$1\text{-}C_4F_8$
C_4F_{10}	Methylcyclo-hexane	$iso\text{-}C_4F_8$
C_5F_{12}		
C_6F_{14}		
C_7F_{16}		

The ion species formed in a mass spectrometric determination of perfluoropropane are shown in Table III.

TABLE III. MASS SPECTRA OF PERFLUOROPROPANE

ion	C	F	CF	CF_2	CF_3	CF_4	C_2F_4	C_2F_5	C_2F_6	C_3F_3	C_3F_5	C_3F_6	C_3F_7	C_3F_8
C_3F_8	2.4	0.98	28.8	9.3	100	--	6.55	9.0	--	0.55	0.23	0.05	24.6	0

Ions are listed in the order of the number of carbon atoms and the number of fluorine atoms in each ion, and intensities are relative to CF_3^+ taken as 100. The most abundant ion is CF_3^+ and the molecule ions are very rare or absent. These results do not seem to contradict the theory that electron bombardment removes fluoride ions from fluorocarbons.

The infrared spectra of fluorocarbons are a potentially useful means of characterization. The infrared spectra of some fluorocarbons have been determined. Many workers (40, 53, 52, 4, 5, 48, 10) have studied perfluoromethane. Infrared absorption curves (40, 52, 4, 5, 48) and Raman spectra (53, 52, 10) have been carefully determined and force constants (14, 39, 24, 44, 18) calculated for the C-F bond. Perfluoropropene, C_3F_6 (37), sulfur hexafluoride, SF_6 (13) and compounds containing the trifluoromethylthio-groups, $CF_3 \cdot S \cdot$ (35) have been studied for the infrared characteristic. Edgell and co-workers (19) have studied the Raman and infrared spectra for perfluoropropane. Little work has been done on other perfluorocarbons.

EXPERIMENTAL

General Description of Corona Cell

The cell used in the determination of corona characteristics for a gas or gas mixture was constructed as shown in Figure 1.

The main body of the cell was made of a glass tubing 20 mm. in diameter with a length varying with the volume needed. The upper electrode was inserted in a 19/38 standard taper joint which was sealed to the main body of the cell. This electrode consisted of a 19/38 standard taper male joint machined from brass. The brass joint was drilled and tapped to accept a one quarter inch NC 20 threaded rod which extended two inches when screwed all the way in the joint. A small knob was brazed on the far end of the rod so that it would ride on a vertical ridge in the glass and prevent the rod from rotating. The rod was held centered by several Vigreux type indentations so that on rotating the brass joint, a movement of one inch could be obtained for every twenty turns. A hole was drilled in the end of the rod and a set screw was placed perpendicular to the hole. A piece of number 18 copper wire was inserted into the hole and held with the set screw. The wire was cut exactly one inch from the rod. The end of the wire was filed flat in order to obtain a reproducible geometry.

The lower electrode was inserted from one end of the main cell which was provided with a 24/40 standard taper female joint. The electrical contact was made by sealing a tungsten wire through the end of a 24/40 standard taper male joint. A rectangular stainless steel

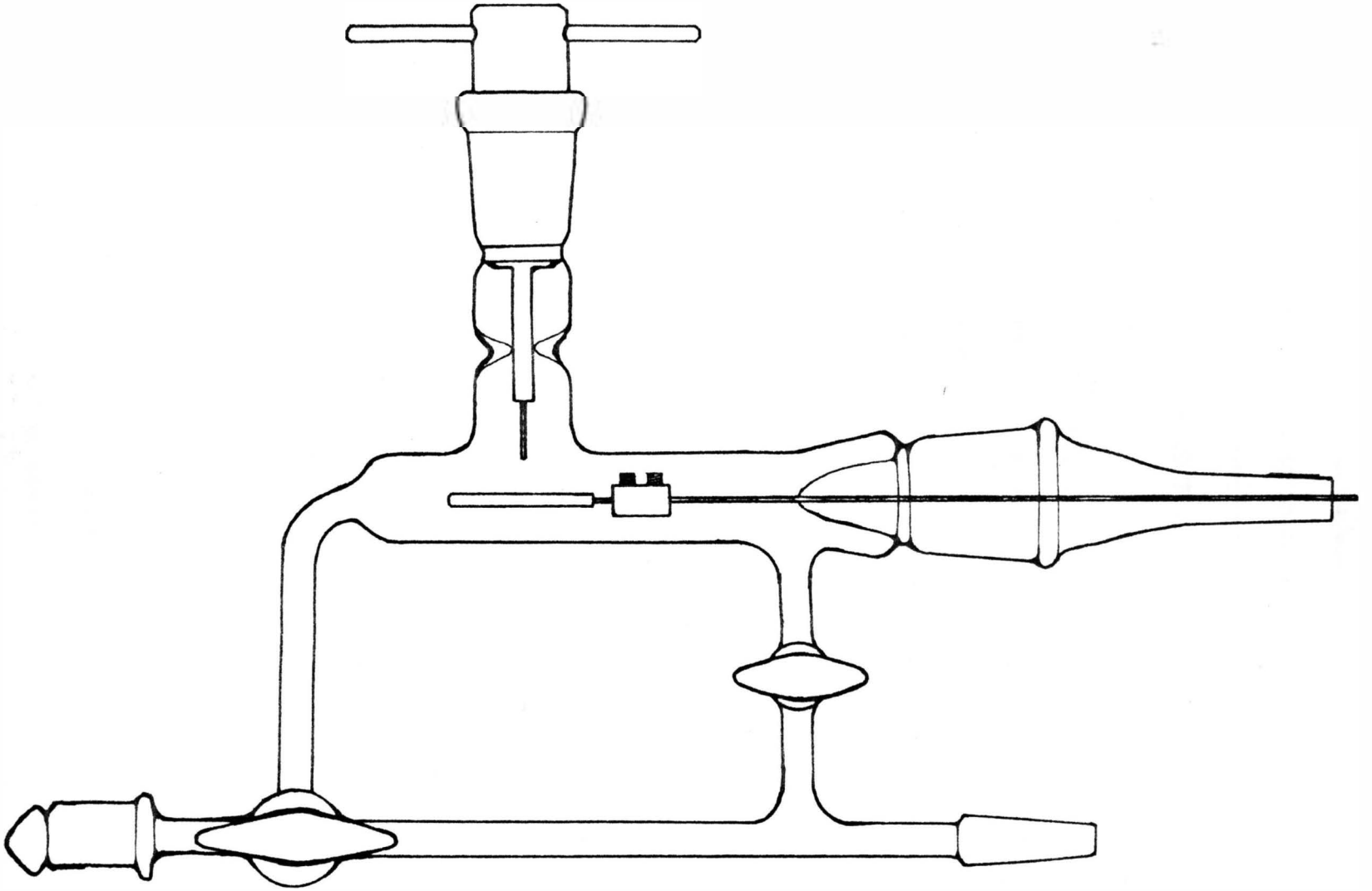


FIGURE 1. CORONA CELL

plate one inch by one half inch was attached to the tungsten wire with a collar on which there were two set screws.

The cell was equipped with two 10/30 standard taper male joints, a Corning type 7420 three way stopcock, and a Corning type 7220 two way stopcock in order to introduce and remove the gas samples.

In the cells used, the electrodes were enclosed in a volume of 42 ml. and a one half inch point to plate gap was used.

Before each run the cell was first washed with benzene then with soap and water, then rinsed with distilled water and finally with acetone. After the electrodes were assembled in place using stopcock grease to lubricate the joints, the cell was evacuated to insure dryness and was then considered ready for use.

Piston Type Gas Mixer

In the beginning, a liquid displacement type gas mixer was tried in order to prepare the gas mixture. However, after several tests, mercury did not prove to be a satisfactory displacing liquid since its vapor contaminated the gas and decreased the breakdown voltage. An organic liquid with a low vapor pressure did not satisfy the requirements because some of the gas dissolved in the organic liquid used as the displacing liquid.

The piston type gas mixer was designed as shown in Figure 2 to overcome the above difficulties. The main cylinder of the mixer was made of a glass tubing 15 mm. in diameter with a length of 80 cm. A five mm. glass tubing was bent and sealed near the top of this cylinder. This tubing which extended to the bottom of the main cylinder was

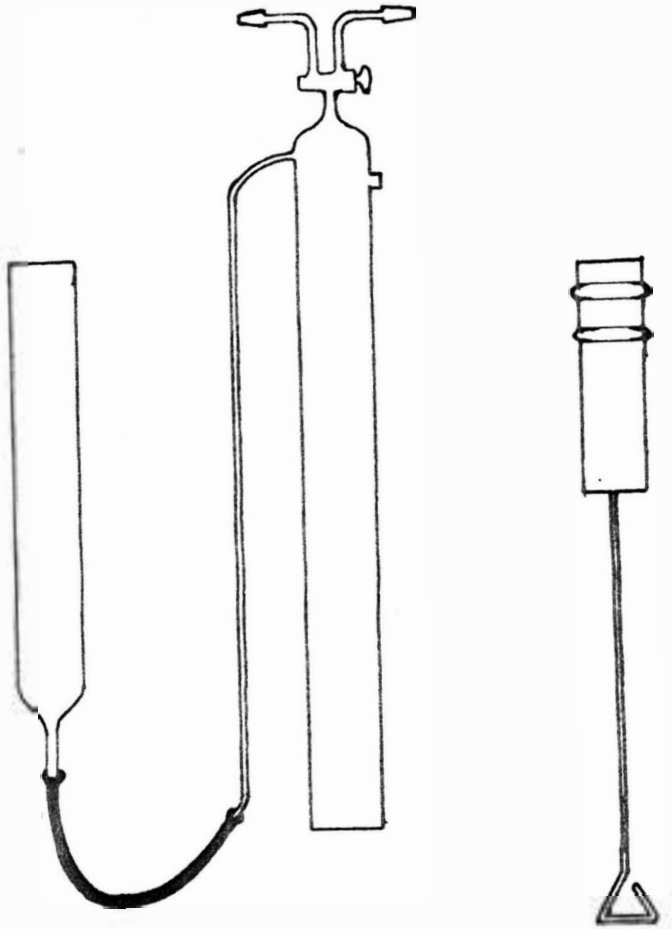


FIGURE 2. PISTON TYPE GAS MIXER

connected with Tygon tubing to a leveling tube. This part acted as a manometer. A rubber serum stopper outlet was put near the top of the cylinder for introducing samples. A Corning type 7380 three way stopcock was sealed at the top end of the cylinder with one arm to the gas tank and another to the cell.

A six inch piston rod was machined from brass with a diameter to fit the main cylinder. Two grooves were made at the top end of the piston to accept two O rings in order to make a gas-tight fit. An iron rod of 4 mm. diameter and long enough to move the piston to the top of the cylinder was used as the handle.

Before calibrating the volume of the main cylinder, it was thoroughly cleaned with chromic acid cleaning solution, rinsed with distilled water and then allowed to dry. The open end of the cylinder in which the piston is normally inserted was connected to the bottom of a 50 ml. buret with rubber tubing. In the calibration process, the buret was clamped in a position such that the bottom of the buret was as high as the top of the cylinder. The rubber tubing was then filled with distilled water and the first calibration level was marked. The stopcock of the buret was now closed and the buret filled with distilled water. After each milliliter of water was allowed to run by gravity from the buret to the cylinder, the appropriate mark was made on the cylinder. The total volume calibrated was again checked by repeating the process.

The piston type gas mixer was assembled using di-n-butyl phthalate as the manometer liquid and glycerine as the lubricating

agent for the piston. One of the outlets on the two way stopcock at the top of the mixer was connected to the sample cell and the other connected to the perfluoropropane tank by means of a rubber hose which was interrupted with a Corning type 7420 three way stopcock and a T tube leading to a liquid type pressure relief valve.

In operating this apparatus, the two way stopcock on the top of the gas mixer was turned to connect the mixer to the tank. The 7420 three way stopcock was turned so that all three openings were connected. The piston was then raised to the highest position. The 7420 stopcock was turned so that the tank and the mixer were connected, but the system was no longer open to the atmosphere. The tank was opened and the excess gas was allowed to escape through the gas relief valve. The piston was then moved up and down for three to five minutes and was finally located at the volume needed. The stopcock was closed at the top of the mixer and the leveling tube was adjusted to bring the gas in the mixer to atmospheric pressure. A calculated amount of sample to be tested for inhibitor properties was injected into the mixer through the rubber stopper. Time was allowed for evaporation when necessary. In order to maintain atmospheric pressure after the addition of the sample, the volume was increased in the mixer by lowering the leveling tube. This lowered both arms of the manometer and effectively increased the volume in the mixer by a small amount. It was found that this was a more satisfactory method for changing the volume by small amounts than by trying to move the piston a short distance.

The corona cell was connected by the 10/30 standard taper joint to the mixer in order to fill it. The cell and its side arms were evacuated. The gas mixture was then delivered into the cell by opening the top stopcock in a way such that a very slow gas velocity could be obtained. The decreasing pressure in the mixer was balanced by gradually moving the piston up so that the system was always kept near atmospheric pressure. At the end, the piston was close to the top position and was adjusted carefully to exactly balance the manometer. The cell after this adjustment was filled with the gas mixture at atmospheric pressure.

Voltage Source and Corona Measurement

The high voltage source and the stress measurement device were set up for use by the Engineering Research Group. As noted in the acknowledgment, the equipment was kindly made available for this part of the project by the courtesy of Prof. Kenneth Lindley and Prof. Perry Williams. The high voltage output from the test set was connected in series to the corona cell and a corona detecting device.

The schematic diagram for the experiment is shown in Figure 3.

It should be emphasized that the term corona as used in this thesis refers to an attempt to estimate the relative number of metastable species and free electrons only. It does not have any significance in relation to the absolute dielectric properties of the gas or gas mixture. The corona detecting device formed a trace on the oscilloscope. This trace was empirically found to increase with increasing transfer of

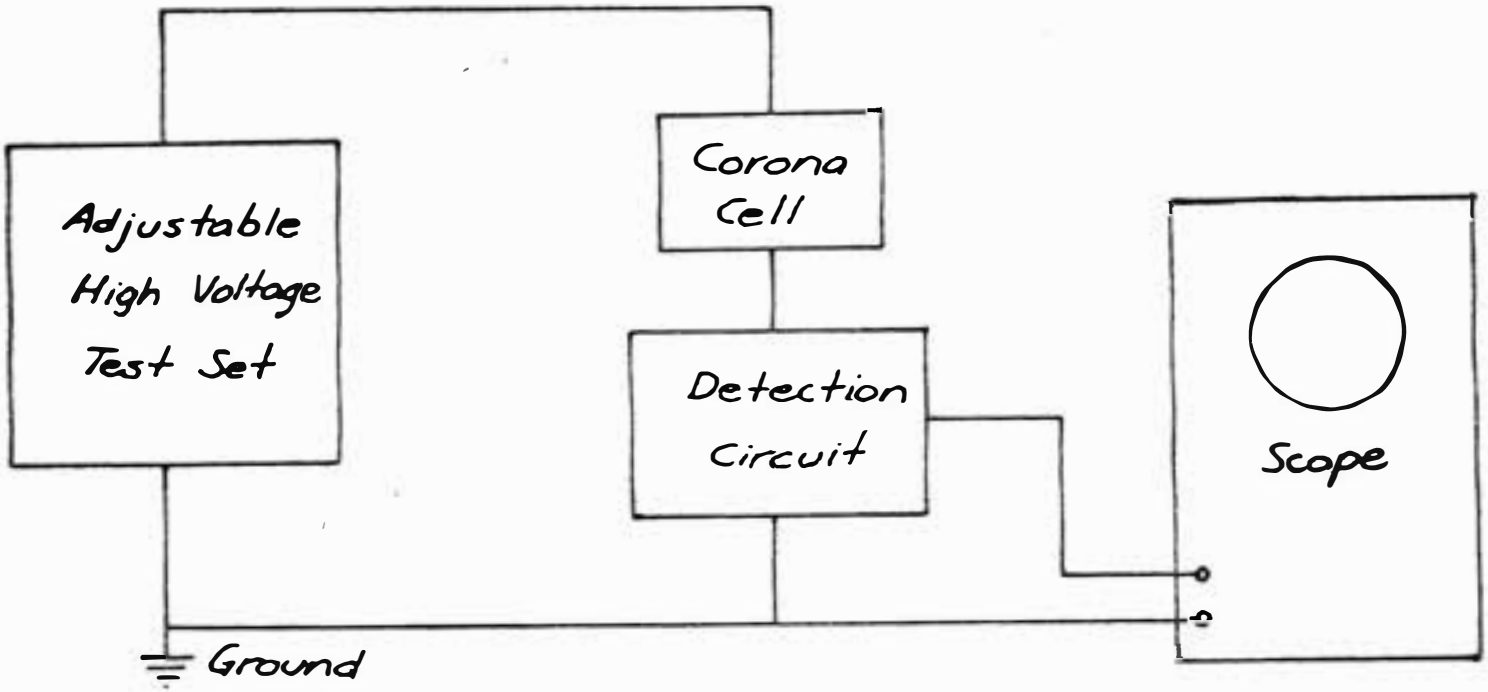


FIGURE 3. CIRCUIT FOR HIGH VOLTAGE TEST

charge between the electrodes of the corona cell. Since it was logical to expect that metastable species and free electrons would also increase with increasing electrical stress, it was assumed that the intensity of the oscilloscope tracings could be used as an uncalibrated measure of the production of these species. Because an uncalibrated measurement of this kind would obviously have arbitrary scales it was decided to correlate the extent of the chemical processes with the average height of the total scope deflection. Since most of the deflection groups involved innumerable spikes, the average was determined by a judging process rather than by mathematical means.

In order to compare the relative amounts of corona for different gases under different applied voltages, a Land Polaroid scope camera was used for taking pictures of the oscilloscope screen. The scope was adjusted to give the brightest reading of the screen in order to enable the scales to be photographed clearly. The intensity was adjusted to give a good picture of the trace of the camera set at 1/50 second at f/1.9 to f/2.8. Polaroid 3000 speed film which takes 10 seconds to process was used.

Method of Analysis

Gas Chromatography

The equipment used for gas chromatography is shown schematically in Figure 4.

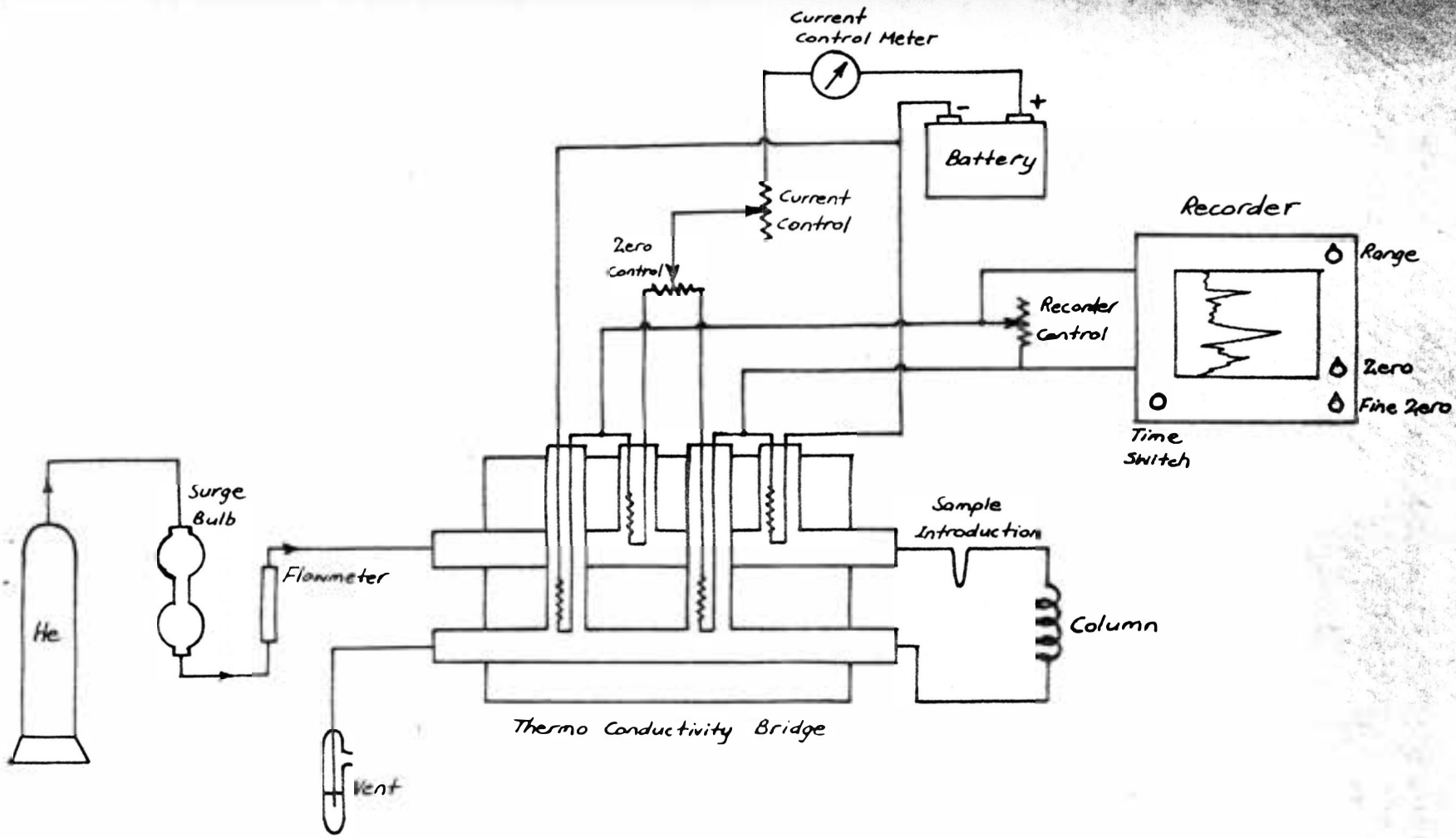


Figure 4. Diagram of Apparatus for Gas Chromatography

The main components of the apparatus can be divided into four sections: the apparatus for supplying and measuring the carrier gas, the system for introducing the sample, the column for separating the components, and the apparatus used for detecting the components in the effluent. These four items will be considered separately.

The first section was the apparatus for supplying and measuring the carrier gas. The helium gas was obtained from a high pressure cylinder through a two stage regulator equipped with a needle valve. The use of dry gas is essential, since water will show up as one of the components in the chromatogram. The gas obtained from the supplier was found to be free of water and was used directly.

The gas was first passed through a 1500 ml. surge bulb to even out the flow. It then passed through a Manostat Corporation Predictability Flowmeter. These flowmeters consist of spherical floats in triflat tubes. These tubes are circular in cross section at the bottom and triangular at the top. The flowmeter was used with a sapphire ball and was capable of flow rate readings from 3.27 ml./sec. to 37.2 ml./sec. For quantitative analysis it is necessary for the flow to be substantially constant, in order that all components recorded on the time axis may be calculated on the same volumetric basis. For qualitative determinations, it is not essential for the flow to be accurately reproducible in the successive separations.

The second section was the system for introducing the sample. The manner in which the sample was introduced into the chromatographic column was of utmost importance owing to its influence on the shape of

the elution peaks. In order to attain sharp peaks the sample is ideally introduced as a "plug".

At first, samples of gases were introduced into the column with a hypodermic syringe using a size 22 needle through a self-sealing serum cap. The cap was on a T at the front end of the column. This was a very rapid and easy procedure. However, in the study of perfluoropropane gas, it was found that the injected gas diffused back into the reference arm of the thermoconductivity cell. The hot tungsten wire in this part of the cell was found to thermally decompose the injected gas. This unwanted reaction produced a second peak in addition to the perfluoropropane peak. This peak was found for every analysis of perfluoropropane regardless of its previous history. The production of this thermal decomposition by-product confused the analysis of the decomposition products produced by the effect of the high voltage stress or corona conditions.

This necessitated a second method of introducing the gas sample. The device illustrated in Figure 5 was found to be convenient. With stopcocks 2 and 3 in the positions shown, the gas stream passes from A to B through stopcock 1 and then on to the column. The U-tube is filled with the sample. The sample is then carried to the column by turning stopcocks 2 and 3 and closing stopcock 1.

The third section was the column for separating the components. The column was made of one fourth inch inside diameter copper tubing. The support was prepared by crushing Johns-Manville C-30 firebrick in iron mortar. The portion which passed through a 60 mesh screen but did

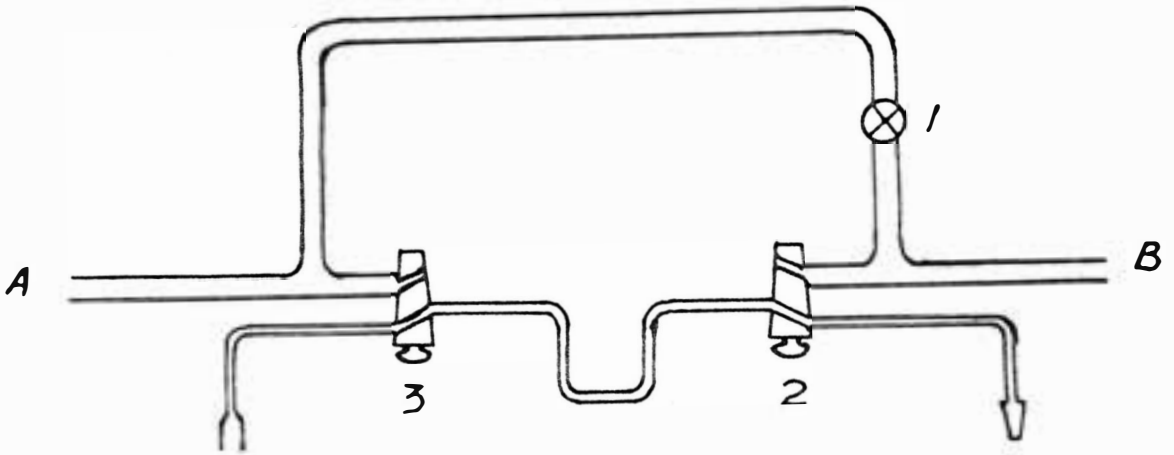


FIGURE 5. SAMPLE INTRODUCTION DEVICE

not pass through an 80 mesh screen was used. The adhering dust was further removed by washing with Skelly B. The washed support was then made into a slurry with dibutylphthalate dissolved in Skelly B. The amount of dibutylphthalate was 20 per cent by weight of the dry brick. The solvent was evaporated on a steam bath with stirring to get an even distribution of the stationary liquid on the support. Agitation was kept gentle so the soft granules were not crushed. The resultant support appeared quite dry and was easily handled. The straight copper tube was held in a vertical position, the bottom was plugged loosely with one half inch of glass wool, and the packing was poured in through a funnel. With the addition of every small portion of support, the entire length of the tube was vibrated by means of a rod inserted in a vibrating type tool generally used to mark metals and glass. This insured evenness of packing throughout the column. The absence of voids was checked by calculating the volume of the tube to be filled and comparing this figure with the amount of packing added. The column, when filled to within one half inch of the top, was plugged with a piece of glass wool. The packed column was coiled around a suitable mandrel of six to eight inches in diameter.

Six, twelve, and twenty-five foot columns were made and used in the gas analysis. The longest column provided the best separation.

The fourth section was the apparatus used for detecting the components in the effluent. One type of a detection instrument which can be used is known as a thermal conductivity cell. The cell used was the pretzel type made by the Gow-Mac Instrument Company. This cell has

two channels each of which contains tungsten wires. The wires are heated by a constant electric current. The conductivity of the surrounding gas is a factor that determines the temperature of the wires and consequently also their resistance. This latter property is measured. Pure helium gas flows through the first channel before entering the column. The gas which has passed through the column flows through the second channel. Any differences in resistance of the two wires due to the effects of volatile components in the effluent are then recorded. The bridge circuit is shown in Figure 6. The two channels are more clearly shown in Figure 4.

The bridge is first balanced with pure helium gas surrounding both channels. When the effluent subsequently becomes admixed with a sample having a different thermal conductivity, the result is an out-of-balance potential between A and B, which can be amplified and recorded on a chart. The recorder used was a Bristol's Model 590 Wide-Strip Dynamaster type with a chart speed of two inches per minute.

To operate the gas chromatography apparatus, the following steps were followed.

1. The helium gas tank was opened and the reducing valve adjusted to give an output pressure of five pounds. The needle valve was adjusted to give a flow rate of about 18 ml./sec. The gas was allowed to flow through the system for at least 15 to 30 minutes in order to establish equilibrium.

2. The voltage was applied to the bridge. The current control was adjusted until 100 milliamperes was obtained.

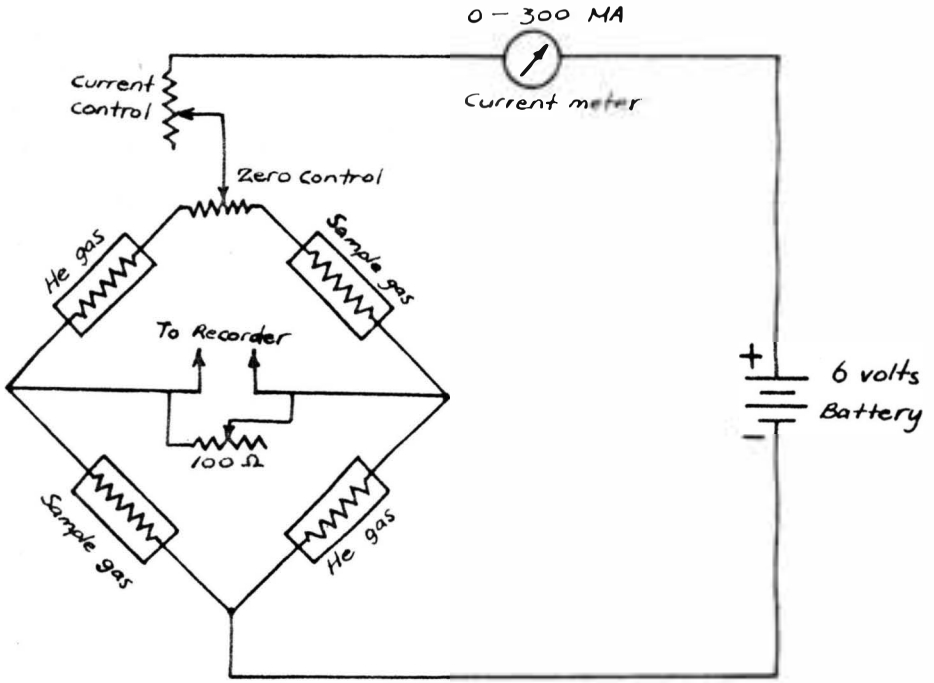


Figure 6. Bridge Circuit

3. The on-off switch of the recorder was turned on one to two minutes before use in order to allow for warm-up time.

4. The zero control knob was adjusted until 0 millivolt was obtained on the millivoltmeter.

5. The stylus of the recorder was brought to the base line by first turning the "Zero" knob and then the "Fine Zero" knob on the recorder.

6. The time switch on the recorder was turned on in order to start the chart. This was to check for stability of the base line while working on step 7.

7. The U-tube was evacuated and the sample introduced.

8. If the base line was found not to be constant, then the helium was allowed to flow until a constant base line was obtained. The stylus was then brought back to the base line by repeating step 5.

9. A suitable height for the peaks was obtained by adjusting both the recorder control and the range switch on the recorder.

10. The U-tube stopcocks were turned as described before and the sample plug was then carried into the column.

Infrared Spectrum

In order to investigate the infrared spectrum of the gas a cell was made as shown in Figure 7.

Cells of 111 mm. and 112 mm. path lengths were made in the following way. A glass tubing 22 mm. in diameter was flared and beaded at both ends and was ground by first using 150 mesh carborundum, then 400 mesh and finally 600 mesh. This was done by mixing a small amount of

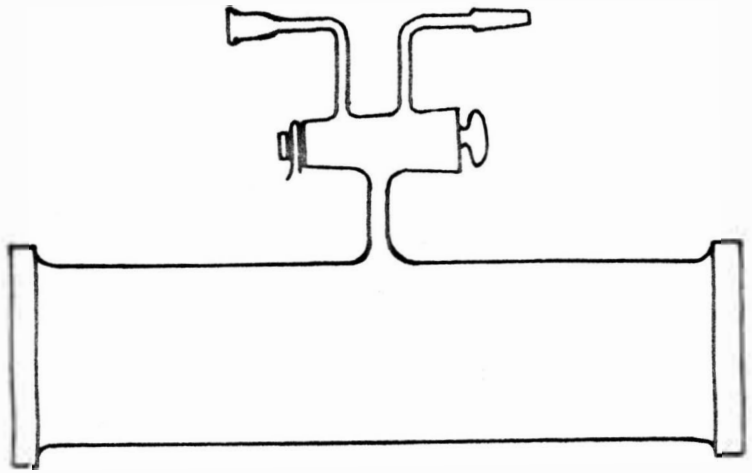


FIGURE 7. INFRARED CELL

the carborundum with water to form a paste on a flat glass surface. The end of the glass tubing was then ground on the paste. After grinding a very smooth and flat ring about 3 mm. wide should be obtained. A Corning type 7380 three way stopcock was then sealed in the middle of the tube. A 10/30 standard taper male joint was sealed to one of the stopcock outlets and a 10/30 standard taper female joint was sealed to the other outlet. Two polished sodium chloride windows of 30 mm. diameter were cemented to the ground ends with Fisher Sealite cement. This was accomplished by setting the glass tubing vertically in a desiccator and placing the sodium chloride window on the ground end which was first coated with a thin application of cement. This end was then allowed to dry in the desiccator for at least one hour before being turned around in order to attach the other window in the same way. The windows attached in this fashion could be removed by soaking the end of the cell in dry benzene for two hours. This was found necessary at times to repolish the etched windows.

After the cell was made, it was evacuated to test for leaks. A blank was also run against air as a preliminary check.

To fill the cell, the 10/30 standard taper female joint was connected to the corona cell or any other vessel containing the gas sample and the 10/30 standard taper male joint was connected to the vacuum pump. The three way stopcock was turned so that the cell and sidearms were all evacuated. The sample was then introduced into the cell by turning the stopcock in that direction.

An infrared blank was run on the cell each time before it was used to make sure that all the previous sample was removed.

Discharge Decomposition

In order to study the effect of electrical discharge on gases the apparatus used was similar to that shown in Figure 1.

The corona cell was connected to the high voltage output of a 25 kv transformer. The voltage was varied by using a variac to control the voltage on the primary of this 25 kv transformer. The cell used for the breakdown studies was similar to that used for the corona studies except that the wire electrode was fixed rather than variable. At first it consisted of a piece of tungsten wire sealed in the end of a 19/38 standard taper male joint. Later the tungsten wire was shortened and a collar with Allen head set screws was prepared so that wires made of different materials could be used.

The tests were conducted by raising the voltage until a breakdown occurred. A stopwatch was used to record the length of time the gas was subjected to the arcing.

The average conditions for testing were 20 seconds at about 12 kv. This varied somewhat on the arbitrary gap of about one fourth inch that was produced by the two fixed electrodes. Prolonged arcing or an increase in intensity of the arc caused the joints holding the electrode to pop out because of the thermal expansion of the gas.

Thermal Decomposition

In the study of thermal decomposition a cell was made as shown in Figure 8.

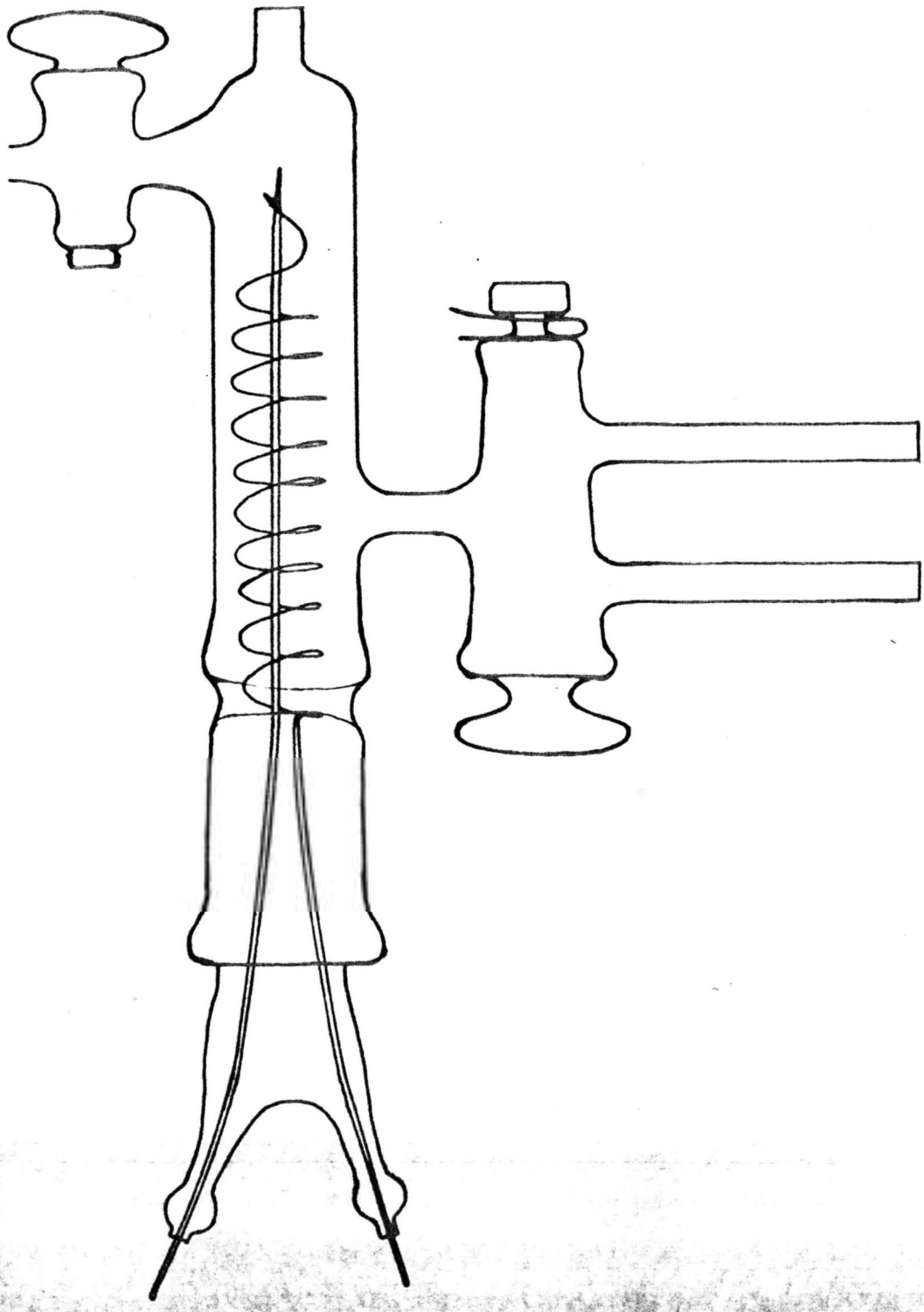


FIGURE 8. THERMAL DECOMPOSITION CELL

A 100 mm. length of glass tubing of 24 mm. diameter was used as the main chamber of the cell. A 24/40 standard taper female joint was sealed on one end, and two tungsten leads of 100 mm. and 50 mm. were sealed separately in the 24/40 standard taper male joint. The longer tungsten lead was insulated by a glass sleeve. The two leads were then connected by spot welding the ends of a 35 cm. length of size 22 Chromel A wire shaped into a coil of about 10 mm. diameter. At the opposite end of the electrodes an outlet with a self-sealing serum cap was attached for sampling. Near this outlet a Corning type 7280 stopcock was sealed and a small toy balloon was attached to allow for gas expansion. At the top of the cell a Corning type 7380 three way stopcock was sealed for introducing and removing samples.

The cell was evacuated by connecting one of the outlets to the vacuum pump. The stopcock leading to the balloon was opened in order to evacuate the balloon and then closed. Gas was introduced into the cell by turning the three way stopcock to the other outlet which was attached to the gas source.

The temperature was controlled by using a variac to control the current flowing through the Chromel A resistance wire. The temperature of the hot filament was determined by using a Leeds and Northrup Model Number 8621 Optical Pyrometer.

The cell was heated by applying voltage to the filament. Meanwhile, the stopcock leading to the balloon was opened slowly so that the gas would be allowed to expand rather than to build up a high pressure in the cell. After cooling, the stopcock was closed and a sample was taken for gas chromatography analysis by using a hypodermic syringe.

RESULTS

Corona

Pure perfluoropropane and its mixtures were investigated for corona at atmospheric pressure and under high voltage. A test cell with a point to plane electrode system with a half inch gap was used. The corona starting voltage for the gas was determined by observing the first disturbance on the oscilloscope before and after exposure to corona. These corona starting voltages are tabulated in Table IV.

The corona characteristics are indicated by plotting the applied voltage against the oscilloscope deflections. The small deflections were caused by the half of the 60 cycle applied voltage which made the wire negative with respect to the plate and the larger deflections by the second half of the cycle in which the plate was negative. The corona observed are shown in Figures 9 through 18. Figures 19 through 37 shows a graphical interpretation of these scope pictures. In experiments where more than two readings were taken, the indication was that the plots would be more or less linear. Whether this is true or not, the important point to note is that the cases where the initial and final points are more nearly vertical and closer to the origin indicate fewer metastable intermediates being formed.

The results of corona characteristics of ethyl methyl sulfide and perfluoropropane of molar ratio 1 to 30 shown in Figure 29 and the mixture thiophene and perfluoropropane of molar ratio 1 to 40 and

TABLE IV. CORONA STARTING VOLTAGES FOR PERFLUOROPROPANE AND MIXTURES

Compounds	Ratio to Perfluoropropane	Corona Starting Voltages (kilo-volts)	Scale Used on the Scope (volts)
Perfluoro-propane		2.5	0.1
Isopropyl Mercaptan	1 : 10	2.1	0.1
"	1 : 20	2.0	0.01
"	1 : 40	6.0	0.1
"	1 : 60	2.5	0.1
Ethyl Methyl Sulfide	1 : 20	2.5	0.1
"	1 : 40	2.5	0.1
"	1 : 30(15 min.)	2.0	0.1
"	1 : 30(1 hr.)	2.0	0.1
"	1 : 30(3 hrs.)	2.5	0.1
"	1 : 30(11 hrs.)	2.5	0.1
Thiophene	1 : 10	2.5	0.01
"	1 : 20	2.5	0.01
"	1 : 40	2.5	1.0
"	1 : 60	9.0	0.1
Dimethyl Disulfide	1 : 10	6.0	0.1
"	1 : 20	7.0	0.1
"	1 : 40	6.5	0.1
"	1 : 60	5.0	0.1

1 to 60 shown in Figures 32 and 33 are the most desirable ones. In these curves, the deflection after corona is much less than before corona using the same applied voltages.

Pure perfluoropropane and the rest of the mixtures all showed similar corona characteristics. In common, these curves after corona exhibit a smaller slope and are located in a position further from the origin than the curve before corona. Therefore, isopropyl mercaptan and dimethyl disulfide as additives did not show an improvement in corona characteristics over that for pure perfluoropropane.

Although the corona characteristics are not shown, carbon disulfide and nitrobenzene were also tested as additives to perfluoropropane. Carbon disulfide seemed to inhibit corona at low voltages but at higher voltages large scope deflections appeared indicating an aggravation of corona over that observed for pure perfluoropropane. A yellow oil was found after exposure of the mixture to corona. Infrared analysis indicated that the oil contained a carbon-carbon double bond and possibly a sulfur-fluorine bond besides the type of bonds initially present. This indicated that both components of the original gas mixture were involved in the formation of the oil. Nitrobenzene did not seem to reduce corona at all. A gummy material was formed on the electrodes indicating some type of reaction. Further work was not carried out on this compound.

Corona Products

In the study of corona products by infrared spectroscopy, an

infrared cell as described in Figure 7 was used to analyze the gas phase samples. Two cells were used. One had a 111 mm. path length, the other a 112 mm. path length. The pressure of gases in these cells was calculated to be about 0.63 atmosphere for all samples unless otherwise stated on the figures showing the data.

Figure 38 shows that the infrared spectra of perfluoropropane before and after corona are similar. The changes noted were in the region 1900-1950 $cm.^{-1}$ where perfluoropropane after exposure to corona showed a change in the height of the peaks, and in the 900-800 $cm.^{-1}$ region where the position of the two absorption bands was shifted and the bands became more intense.

The results of exposing a mixture of isopropyl mercaptan and perfluoropropane to corona are shown in Figure 39 and Figure 40. On decreasing the mole fraction of isopropyl mercaptan, the 3000 $cm.^{-1}$ band became weaker and finally disappeared. The 2300 $cm.^{-1}$ band became more intense, and the peaks between the 1850-1670 $cm.^{-1}$ region started to merge together.

The infrared spectra of the pure perfluoropropane, pure ethyl methyl sulfide, and the mixture of ethyl methyl sulfide and perfluoropropane of molar ratio 1 to 20 are shown in Figure 41. These spectra were determined before exposing these gases to corona. The only band characteristic of ethyl methyl sulfide which was not masked by the perfluoropropane bands was the carbon-hydrogen stretching peak at 3000 $cm.^{-1}$.

The infrared spectra after exposure to corona of the mixture of ethyl methyl sulfide and perfluoropropane in various ratios are shown in Figure 42 and Figure 43. An interesting feature is the band at 2300 $cm.^{-1}$. This band became more intense with a dilution of the ethyl methyl sulfide. However, with no ethyl methyl sulfide present the pure perfluoropropane after corona exhibited only a weak absorption at this point. See Figure 38. In the 900-800 $cm.^{-1}$ region the mixture of ethyl methyl sulfide and perfluoropropane of molar ratio 1 to 10 showed a shift in the position and an intensification of the two absorption bands. In the mixtures of molar ratios 1 to 20 and 1 to 40 the bands between 2600-1400 $cm.^{-1}$ were decreased whereas there were many individual peaks in the 1400-1100 $cm.^{-1}$ region.

The effects of changing the corona exposure time to the mixture of ethyl methyl sulfide to perfluoropropane of molar ratio 1 to 30 are shown in Figure 44 and Figure 45. A band at 3200 $cm.^{-1}$ was found in the sample exposed to corona for 15 minutes. That this absorption was due to a transient species was indicated by the disappearance of this band when corona time was prolonged to 30 minutes. Another band was found at 2300 $cm.^{-1}$ in all of the samples. This absorption was proportional to the corona time.

It was found that in the infrared spectra of mixtures exposed to corona for 11 hours the peaks in the 2800-1400 $cm.^{-1}$ region became similar to that of the pure perfluoropropane before corona.

The effect of adding thiophene to perfluoropropane is shown in Figure 46 and Figure 47. The top two spectra in Figure 46 are for

perfluoropropane and thiophene before exposure to corona. The bottom spectrum in Figure 46 and the spectra in Figure 47 are obtained for varying mixtures of thiophene and perfluoropropane after exposure to corona. The mixtures after corona showed absorptions in the 5000-950 $cm.^{-1}$ region similar to the pure perfluoropropane. A broad absorption band was found in the 900-650 $cm.^{-1}$ region for the mixture of thiophene and perfluoropropane of molar ratio 1 to 10. On decreasing the mole fraction of thiophene, this region started to resolve into individual peaks. The same interesting feature was found for this mixture at 2300 $cm.^{-1}$ as was found for ethyl methyl sulfide and perfluoropropane. Another change was observed at 2050 $cm.^{-1}$. The intensity of this band seemed to be proportional to the amount of thiophene present. In the thiophene to perfluoropropane molar ratio 1 to 60, a small band appeared in the 1950-1900 $cm.^{-1}$ region which was not noted in the other spectra. In general the addition of thiophene seemed to depress the intensity of the perfluoropropane bands in the 5000-1400 $cm.^{-1}$ region more than expected by a Beer's law factor.

The effects of adding dimethyl disulfide to perfluoropropane are shown in Figure 48 and Figure 49. A twin peak was found in the 3700-3600 $cm.^{-1}$ region. This peak appeared to be constant in all the different molar ratios of the mixture. Both bands of 2300 $cm.^{-1}$ and 895 $cm.^{-1}$ became more intense with an increase in dilution of the dimethyl disulfide.

Perfluoropropane Exposed to an Arc Discharge

Nature of Wire Electrode

In the study of electrical discharges on perfluoropropane, either copper, iron or tungsten wire was used as one electrode and a stainless steel plate as the other electrode. The conditions used were a point to plane gap of 0.15 inch, an arcing time of 20 seconds, with about 12 kv of applied voltage. Under these conditions, iron and tungsten produced a turbulent arc between the electrodes and caused the transformer to make extraneous noises. It was feared that the transformer might be damaged under these conditions so the use of these electrode materials was discontinued. Using the copper wire electrode, the arc was much smoother and the transformer operated more normally.

Another difference shown by the copper, iron and tungsten electrodes was the amount of black residue formed on the surface of the stainless steel plate electrode. This black residue was thought to be carbon since there was no carbon-fluorine absorption indicated in the infrared. The amount of carbon formed in 20 seconds when using the copper electrode was 0.0005 g. Even though this was a small amount it was definitely less than that formed in an equal time using the other two metals. When iron was used, 0.0012 g. of carbon was collected, and when tungsten was used 0.0011 g. was collected.

It was concluded that copper was the best material to use for the point electrode.

Gas Chromatography Analysis

The gas chromatography curves of perfluoropropane exposed to discharge using copper, iron and tungsten electrodes are shown in Figure 50. The similar chromatograms indicated that the electrode material did not appreciably affect the gaseous decomposition products of perfluoropropane. Each of these chromatograms showed a high peak of unreacted perfluoropropane and two smaller peaks which might be perfluoromethane, perfluoroethane, perfluoroethylene or some other degradation product. Because the pure perfluorocarbon compounds were not available for comparative purposes the products formed could not be identified.

Fluorine Formation

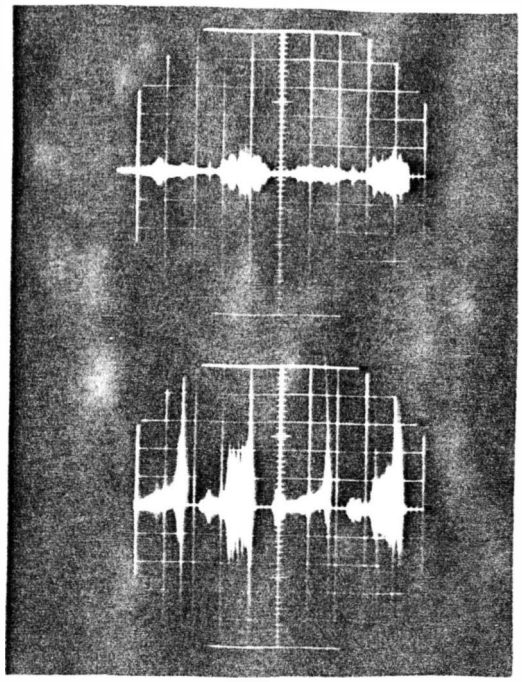
The perfluoropropane gas subjected to an arc discharge was bubbled into potassium iodide-starch solution. This solution rapidly turned a dark blue indicating the possible presence of fluorine.

Thermal Decomposition Products

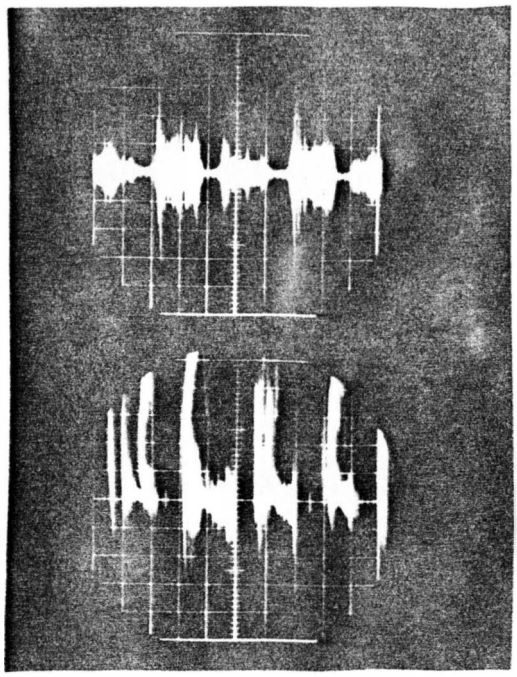
Because the arc discharge produced so much heat, it was desirable to separate the thermal effect from the electrical effects. Perfluoropropane was heated in the thermal decomposition cell for two minutes at each of four different temperatures. These temperatures as determined by the optical pyrometer were 844°C., 954°C., 906°C. and 922°C. with probable error of plus or minus three degrees centigrade. The gas in the cell was then analyzed by gas chromatography. The results are shown

in Figure 51. In the temperature range 844 to 854°C. only the perfluoropropane peak was observed. At 906°C., a second peak was formed with a longer appearance time than perfluoropropane. At 922°C., two peaks other than perfluoropropane were formed. Higher temperatures could not be used since the thermal expansion of the gas as well as the increase in volume due to the formation of decomposition products popped out the standard taper joints in the cell. The volume increase due to the formation of decomposition products was also observed by Wilson (51).

Visible differences were easily observable at the different temperatures. At 844°C. to 854°C., nothing changed except that the resistance wire lost its shiny color and turned to gray. At 906°C., a small amount of white smoke was formed which, after cooling, deposited as a film on the walls of the cell. The filament was also coated by some black residue. At 922°C., a considerable amount of white smoke was formed which made the use of the optical pyrometer quite difficult. This white smoke was not analyzed. The important result was that the gaseous products formed in the low temperature pyrolysis reactions were similar to the gaseous products formed in the arc discharge.



CORONA AT START OF TEST
TOP 5 KV APPLIED VOLTAGE
0.01 V/CM SCALE
BOTTOM 15 KV APPLIED V.
1.0 V/CM SCALE

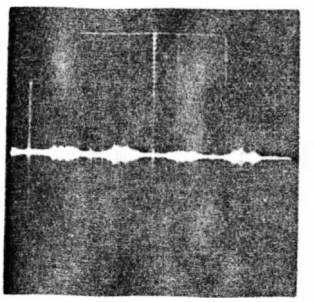


CORONA AFTER 7 HOURS
TOP 15 KV APPLIED VOLTAGE
1.0 V/CM SCALE
BOTTOM 5 KV APPLIED V.
1.0 V/CM SCALE

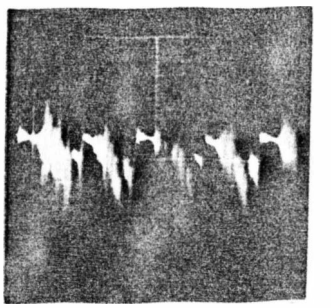
FIGURE 9. CORONA CHARACTERISTICS OF CARBON DISULFIDE AND PERFLUOROPROPANE OF UNKNOWN MOLAR RATIO

Molar ratio isopropyl mercaptan to perfluoropropane 1 to 10

Corona at the start of test

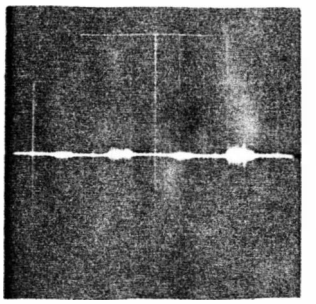


5 kv applied voltage
0.1 v/scale division

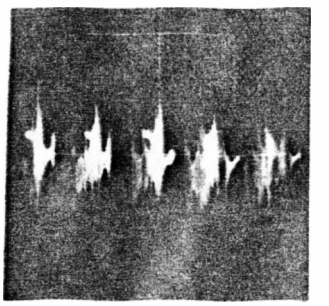


15 kv applied voltage
0.1 v/scale division

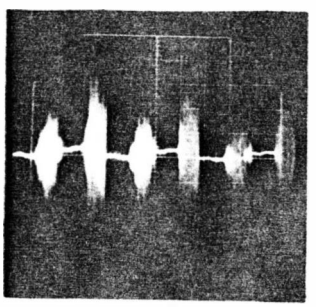
Corona after 2 hrs. 40 min.



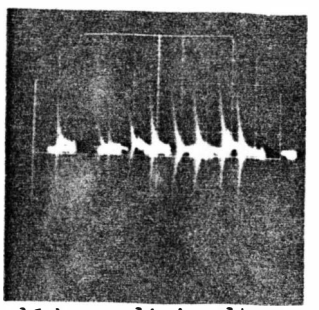
5 kv applied voltage
0.1 v/scale division



15 kv applied voltage
0.1 v/scale division



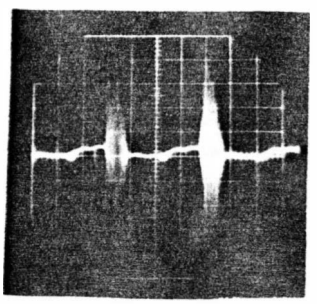
5 kv applied voltage
0.01 v/scale division



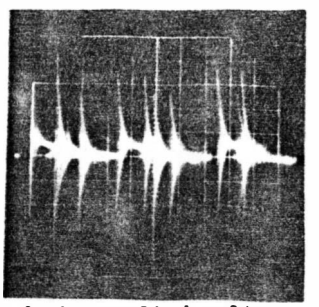
15 kv applied voltage
1 v/scale division

Molar ratio isopropyl mercaptan to perfluoropropane 1 to 20

Corona at the start of test



5 kv applied voltage
0.1 v/scale division



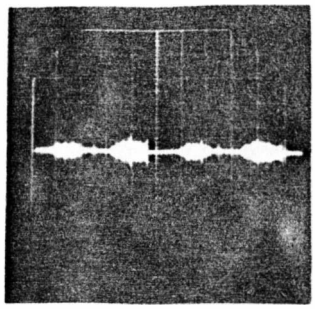
15 kv applied voltage
1 v/scale division

Corona after 3 hrs.

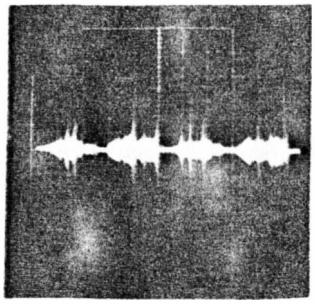
FIGURE 10· CORONA CHARACTERISTICS OF ISOPROPYL MERCAPTAN AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 10 & 1 TO 20

Molar ratio isopropyl mercaptan to perfluoropropane 1 to 40

Corona at the start of test

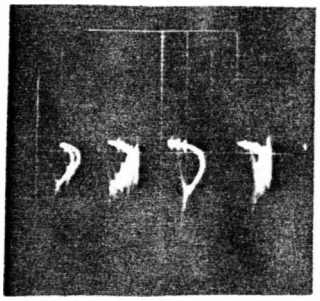


10 kv applied voltage
0.1 v/scale division

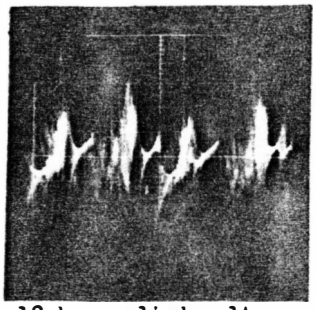


18 kv applied voltage
0.1 v/scale division

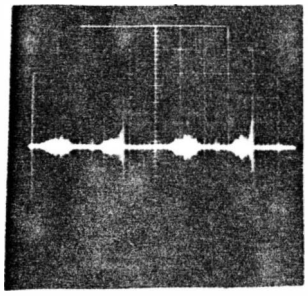
Corona after 2 hrs. 25 min.



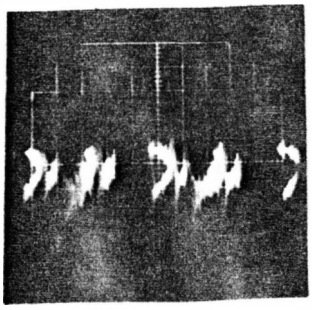
10 kv applied voltage
0.1 v/scale division



18 kv applied voltage
0.1 v/scale division



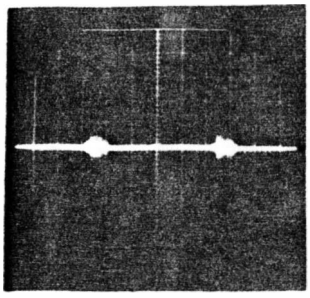
5 kv applied voltage
0.1 v/scale division



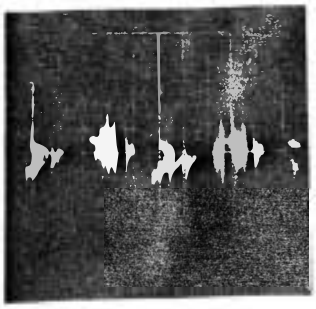
10 kv applied voltage
0.1 v/scale division

Molar ratio isopropyl mercaptan to perfluoropropane 1 to 60

Corona at the start of test



5 kv applied voltage
0.1 v/scale division



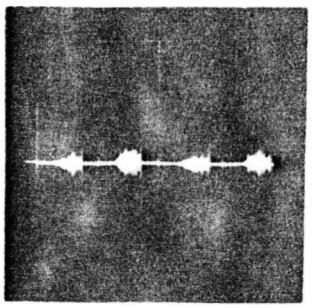
18 kv applied voltage
0.1 v/scale division

Corona after 2 hrs. 30 min.

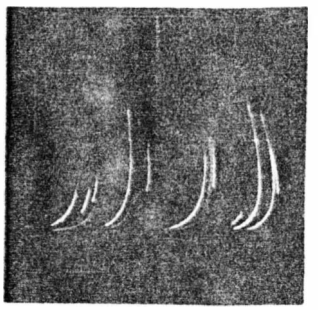
FIGURE 11· CORONA CHARACTERISTICS OF ISOPROPYL MERCAPTAN AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 40 & 1 TO 60

Molar ratio ethyl methyl sulfide to perfluoropropane 1 to 20

Corona at the start of test

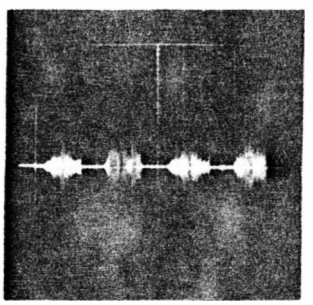


5 kv applied voltage
0.1 v/scale division

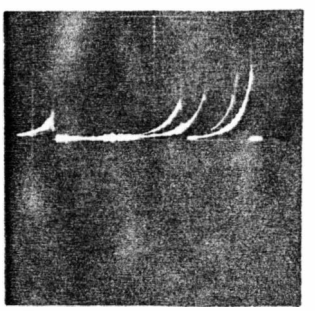


16 kv applied voltage
10 v/scale division

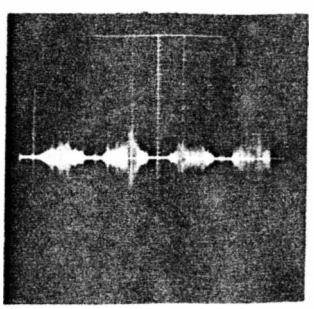
Corona after 8 hrs. 30 min.



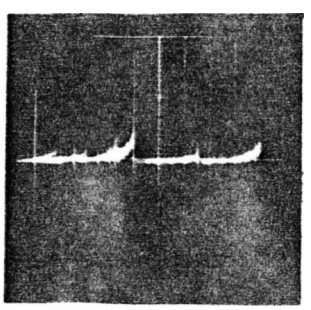
5 kv applied voltage
0.1 v/scale division



6 kv applied voltage*
1 v/scale division



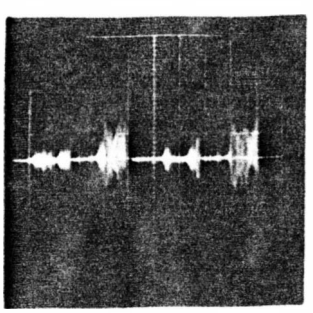
5 kv applied voltage
0.1 v/scale division



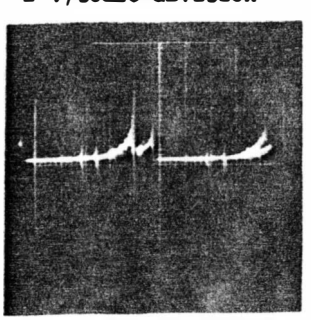
9 kv applied voltage*
1 v/scale division

Molar ratio ethyl methyl sulfide to perfluoropropane 1 to 40

Corona at the start of test



5 kv applied voltage
0.1 v/scale division



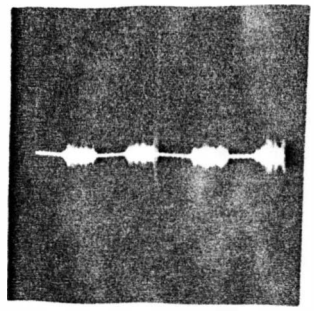
9 kv applied voltage
1 v/scale division

Corona after 11 hrs. 30 min.

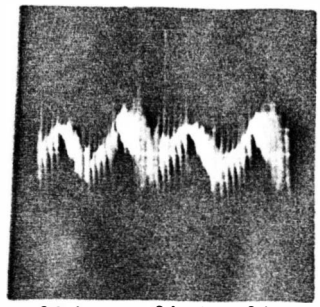
FIGURE 12· CORONA CHARACTERISTICS OF ETHYLMETHYLSULFIDE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 20 & 1 TO 40

Molar ratio ethyl methyl sulfide to perfluoropropane 1 to 30

Corona at the start of test

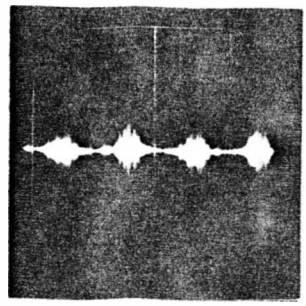


5 kv applied voltage
0.1 v/scale division

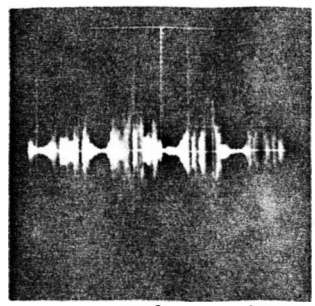


15 kv applied voltage
0.1 v/scale division

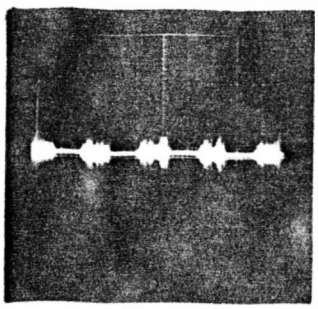
Corona after 15 min.



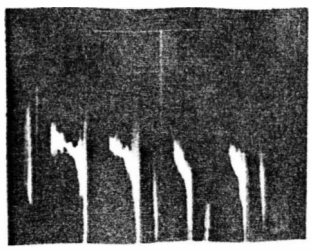
5 kv applied voltage
0.1 v/scale division



15 kv applied voltage
0.1 v/scale division



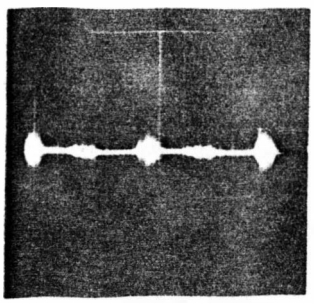
5 kv applied voltage
0.1 v/scale division



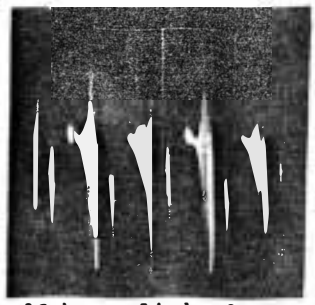
15 iv applied voltage
0.1 v/scale division

Molar ratio ethyl methyl sulfide to perfluoropropane 1 to 30

Corona at the start of test



5 kv applied voltage
0.1 v/scale division

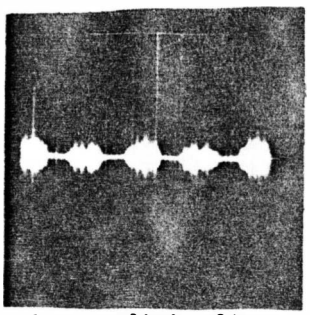


15 kv applied voltage
0.1 v/scale division

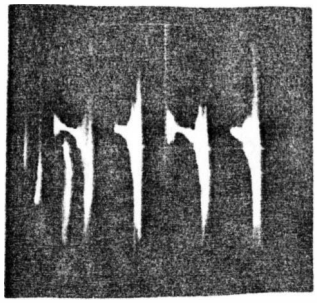
Corona after 1 hr.

FIGURE 13. CORONA CHARACTERISTICS OF ETHYL METHYL SULFIDE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 30

Corona at the start of test

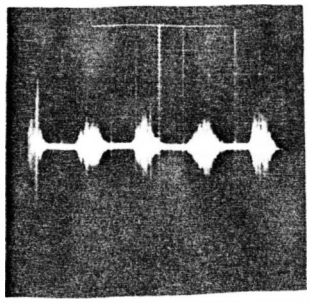


5 kv applied voltage
0.1 v/scale division

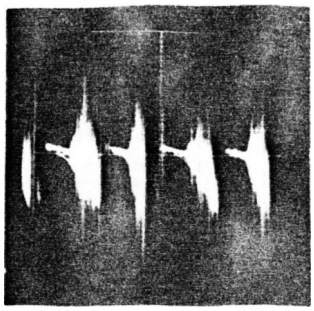


12.5 kv applied voltage
0.1 v/scale division

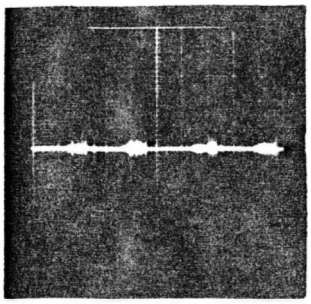
Corona after 3 hrs.



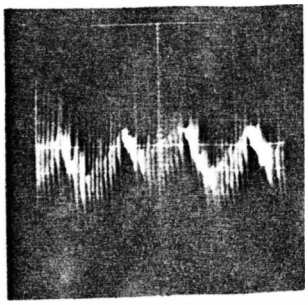
5 kv applied voltage
0.1 v/scale division



10 kv applied voltage*
0.1 v/scale division

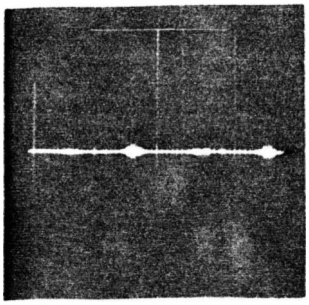


5 kv applied voltage
0.1 v/scale division

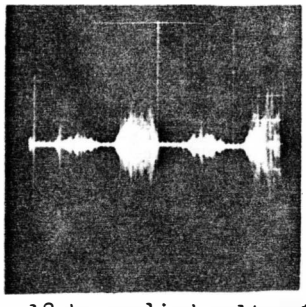


18 kv applied voltage
0.1 v/scale division

Corona at the start of test



18 kv applied voltage
0.1 v/scale division



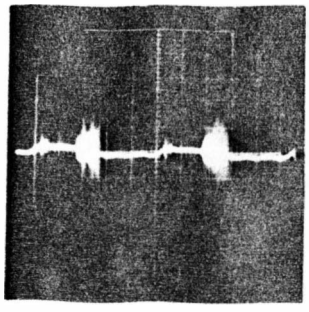
18 kv applied voltage*
0.1 v/scale division

Corona after 11 hrs.

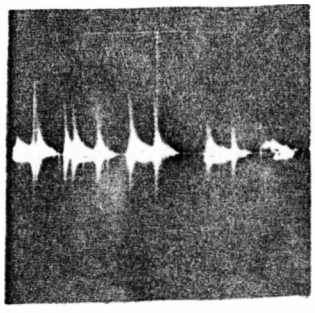
FIGURE 14· CORONA CHARACTERISTICS OF ETHYLMETHYLSULFIDE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 30

Molar ratio thiophene to perfluoropropane 1 to 10

Corona at the start of test

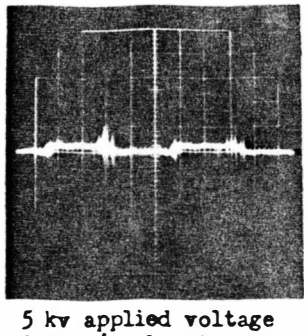


5 kv applied voltage
0.01 v/scale division

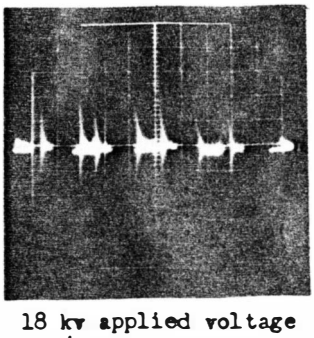


18 kv applied voltage
1 v/scale division

Corona after 2 hrs. 45 min.



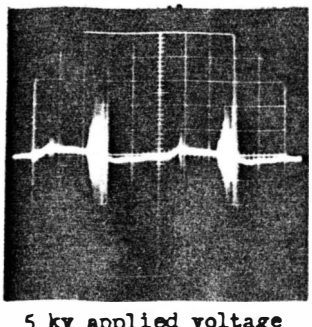
5 kv applied voltage
0.01 v/scale division



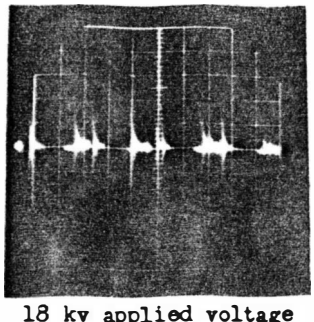
18 kv applied voltage
1 v/scale division

Molar ratio thiophene to perfluoropropane 1 to 20

Corona at the start of test

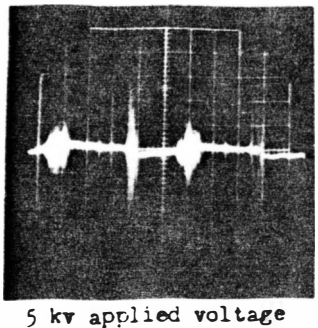


5 kv applied voltage
0.01 v/scale division

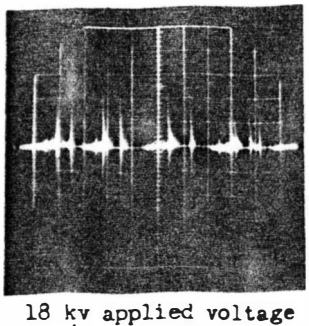


18 kv applied voltage
1 v/scale division

Corona after 3 hrs. 15 min.



5 kv applied voltage
0.01 v/scale division

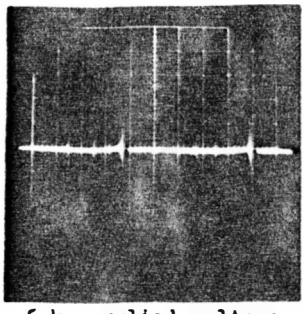


18 kv applied voltage
1 v/scale division

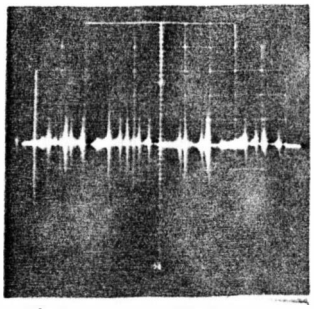
FIGURE 15. CORONA CHARACTERISTICS OF THIOPHENE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 10 & 1 TO 20

Molar ratio thiophene to perfluoropropane 1 to 40

Corona at the start of test

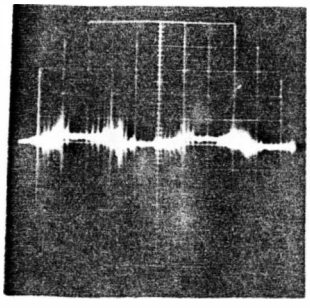


5 kv applied voltage
1 v/scale division

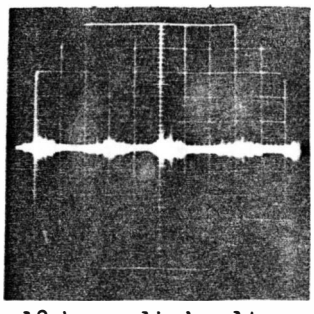


18 kv applied voltage
1 v/scale division

Corona after 3 hrs. 50 min.



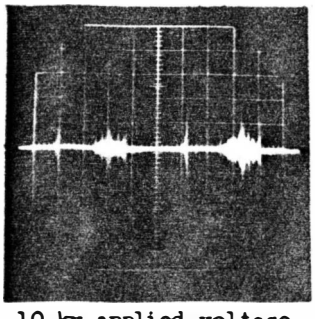
5 kv applied voltage
0.1 v/scale division



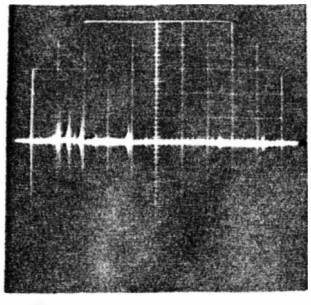
18 kv applied voltage
1 v/scale division

Molar ratio thiophene to perfluoropropane 1 to 60

Corona at the start of test

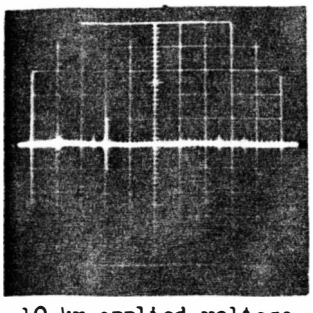


10 kv applied voltage
0.1 v/scale division

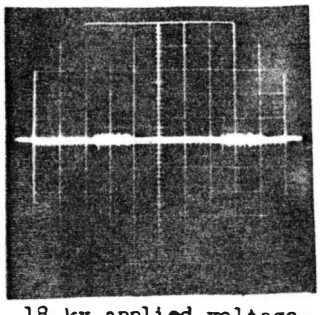


18 kv applied voltage
1 v/scale division

Corona after 3 hrs. 20 min.



10 kv applied voltage
0.1 v/scale division

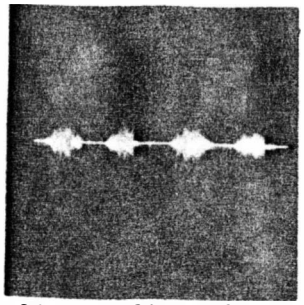


18 kv applied voltage
1 v/scale division

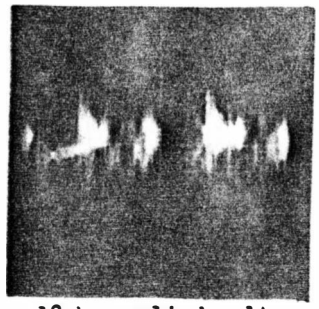
FIGURE 16· CORONA CHARACTERISTICS OF THIOPHENE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 40 & 1 TO 60

Molar ratio dimethyl disulfide to perfluoropropane 1 to 10

Corona at the start of test

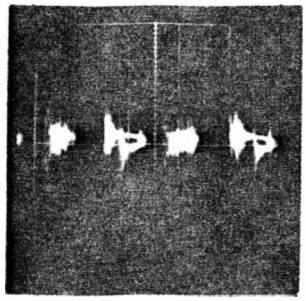


10 kv applied voltage
0.1 v/scale division

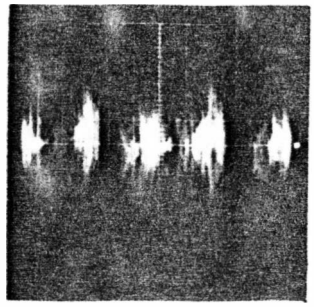


18 kv applied voltage
0.1 v/scale division

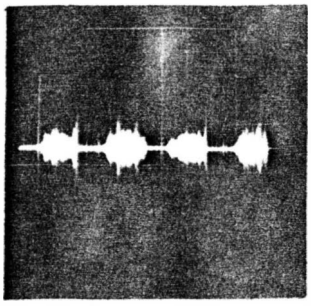
Corona after 3 hrs.



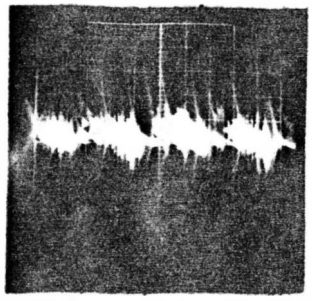
10 kv applied voltage
0.1 v/scale division



15 kv applied voltage*
0.1 v/scale division



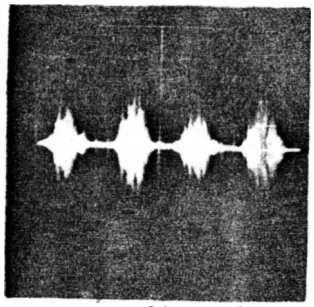
10 kv applied voltage
0.1 v/scale division



18 kv applied voltage
1 v/scale division

Molar ratio dimethyl disulfide to perfluoropropane 1 to 20

Corona at the start of test



10 kv applied voltage
0.1 v/scale division

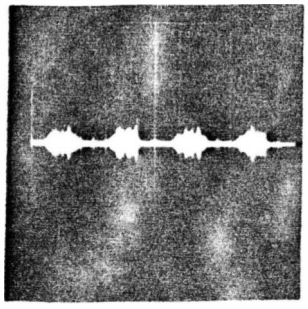
11 kv applied voltage*
1 v/scale division

Corona after 8 hrs. 45 min.

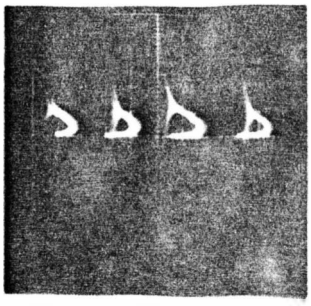
FIGURE 17. CORONA CHARACTERISTICS OF DIMETHYL DISULFIDE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 10 & 1 TO 20

Molar ratio dimethyl disulfide to perfluoropropane 1 to 40

Corona at the start of test

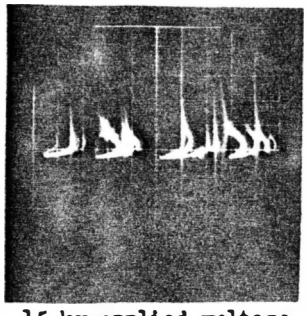


10 kv applied voltage
0.1 v/scale division

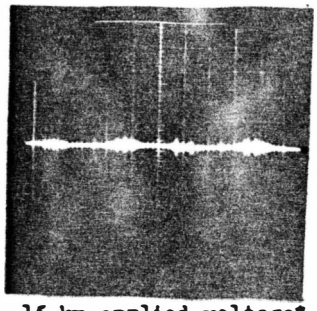


15 kv applied voltage
1 v/scale division

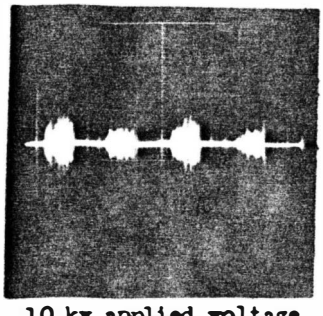
Corona after 3 hrs. 55 min.



15 kv applied voltage
1 v/scale division



15 kv applied voltage*
1 v/scale division

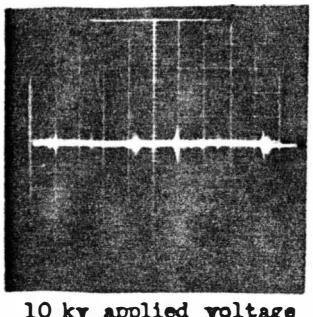


10 kv applied voltage
0.1 v/scale division

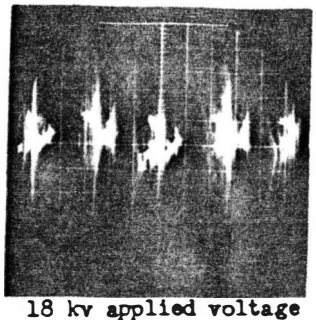
18 kv applied voltage
0.1 v/scale division

Molar ratio dimethyl disulfide to perfluoropropane 1 to 60

Corona at the start of test



10 kv applied voltage
0.1 v/scale division



18 kv applied voltage
0.1 v/scale division

Corona after 3 hrs. 15 min.

FIGURE 18· CORONA CHARACTERISTICS OF DIMETHYL DISULFIDE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 40 & 1 TO 60

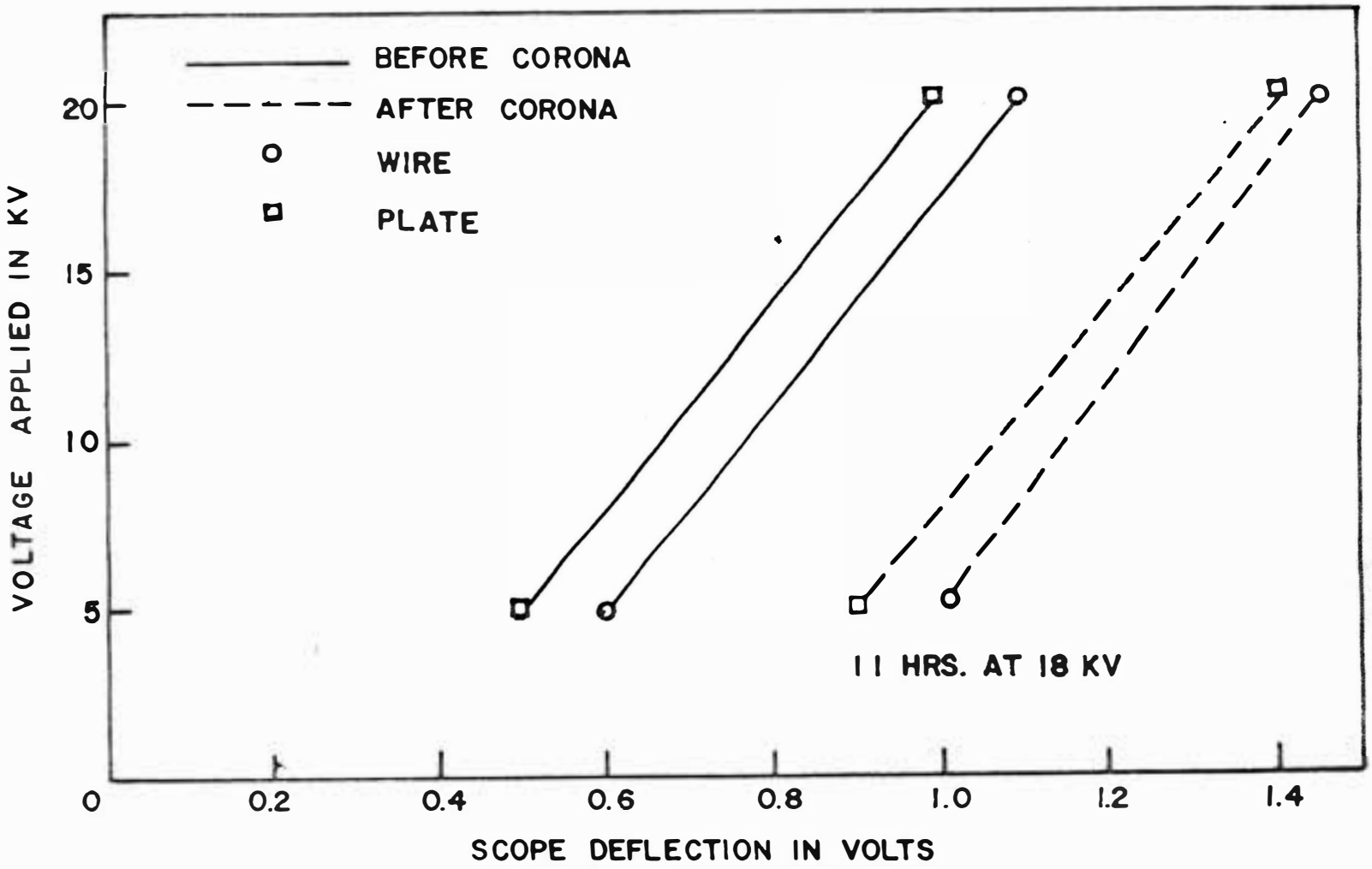


FIGURE 19. CORONA CHARACTERISTICS OF PURE PERFLUOROPROPANE

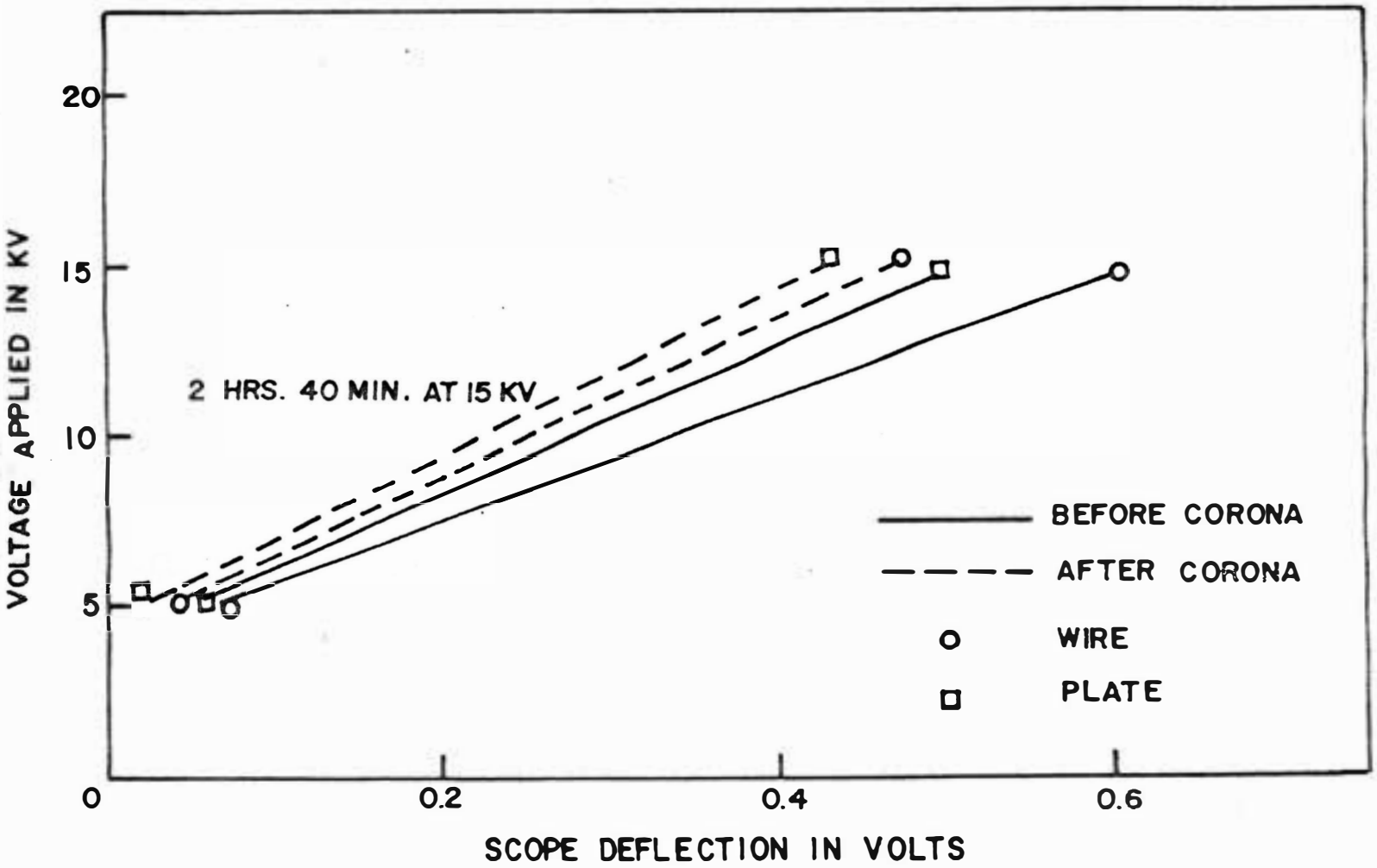


FIGURE 20. CORONA CHARACTERISTICS OF ISOPROPYL MERCAPTAN AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 10

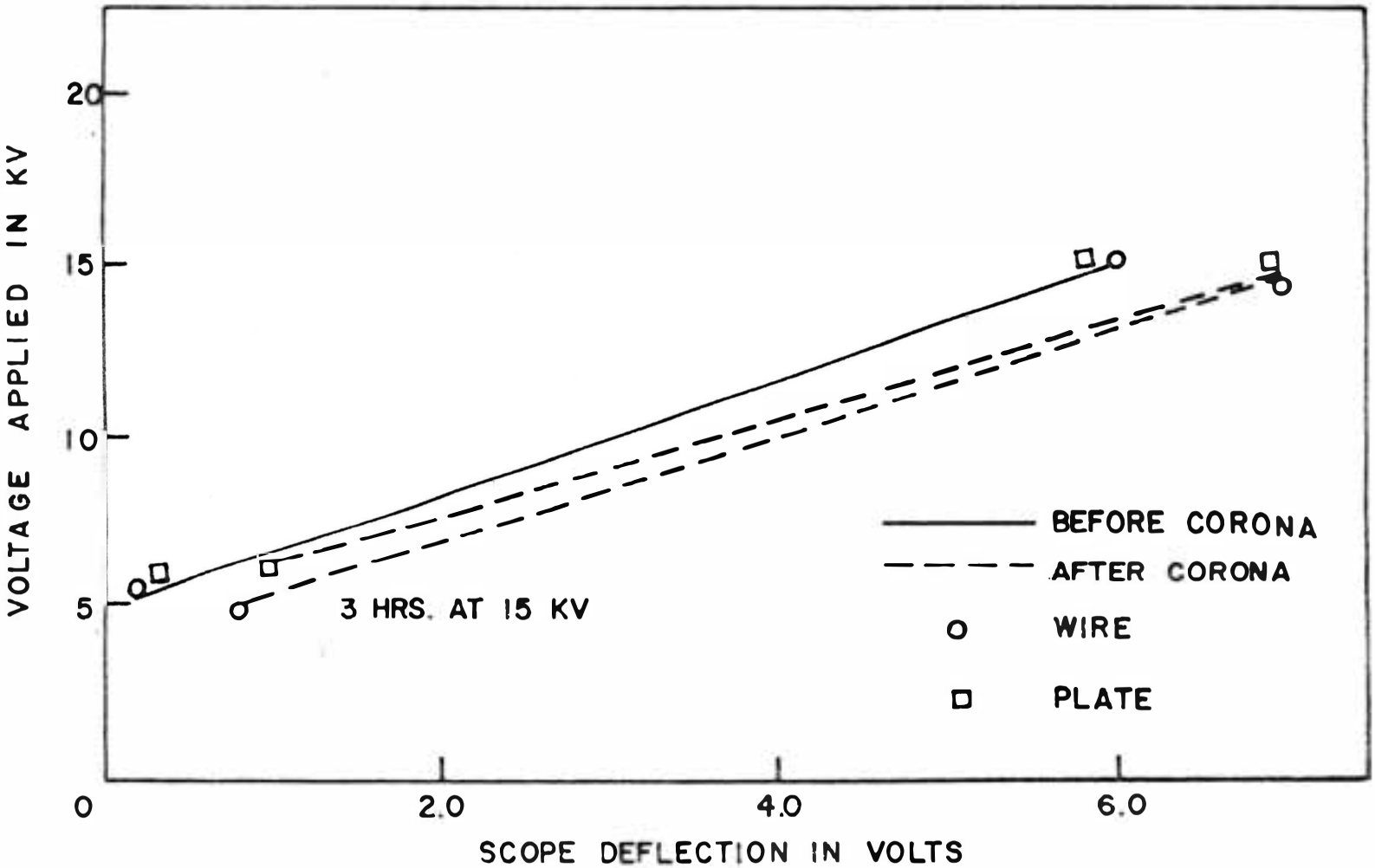


FIGURE 21. CORONA CHARACTERISTICS OF ISOPROPYL MERCAPTAN AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 20

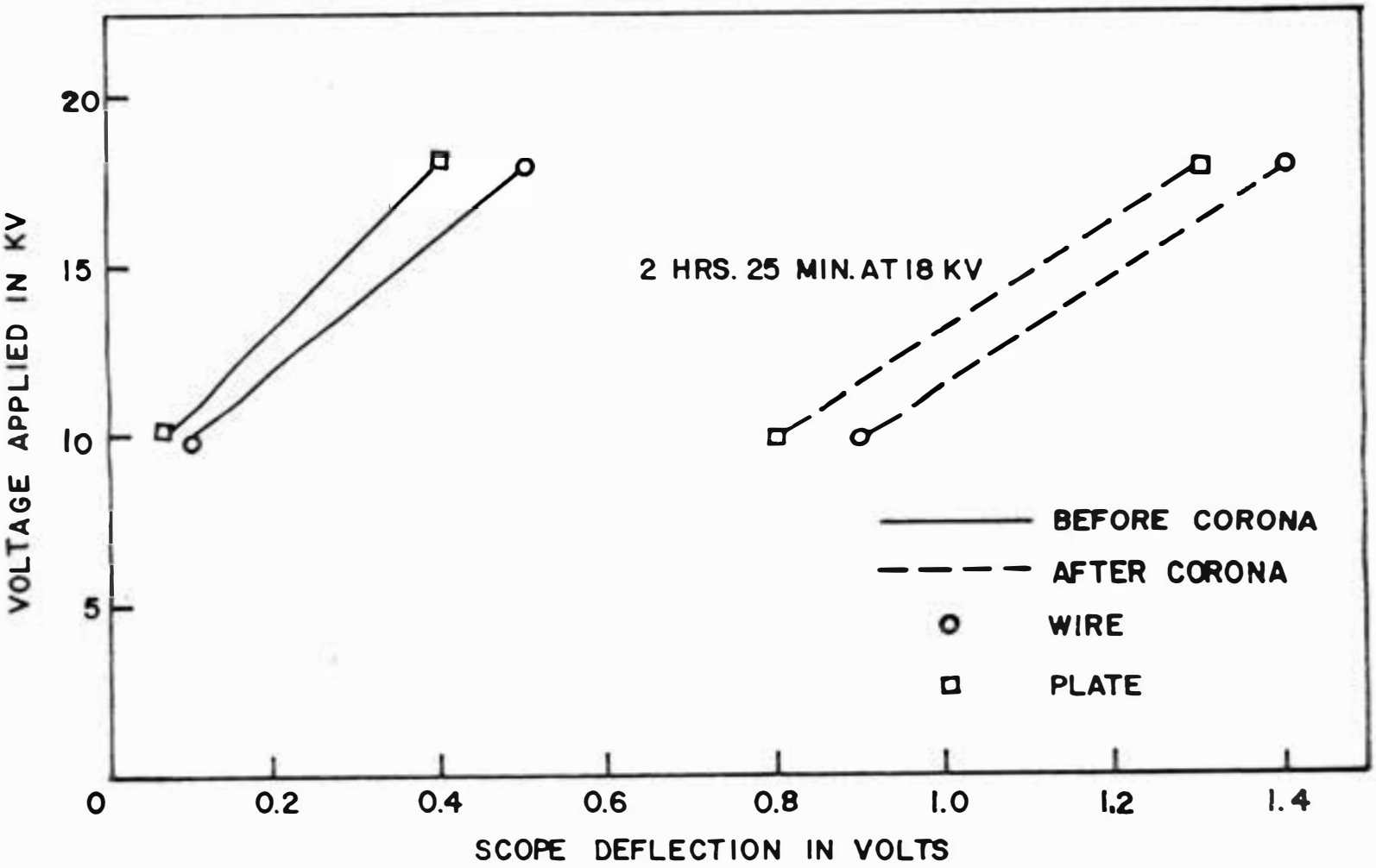


FIGURE 22. CORONA CHARACTERISTICS OF ISOPROPYL MERCAPTAN AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 40

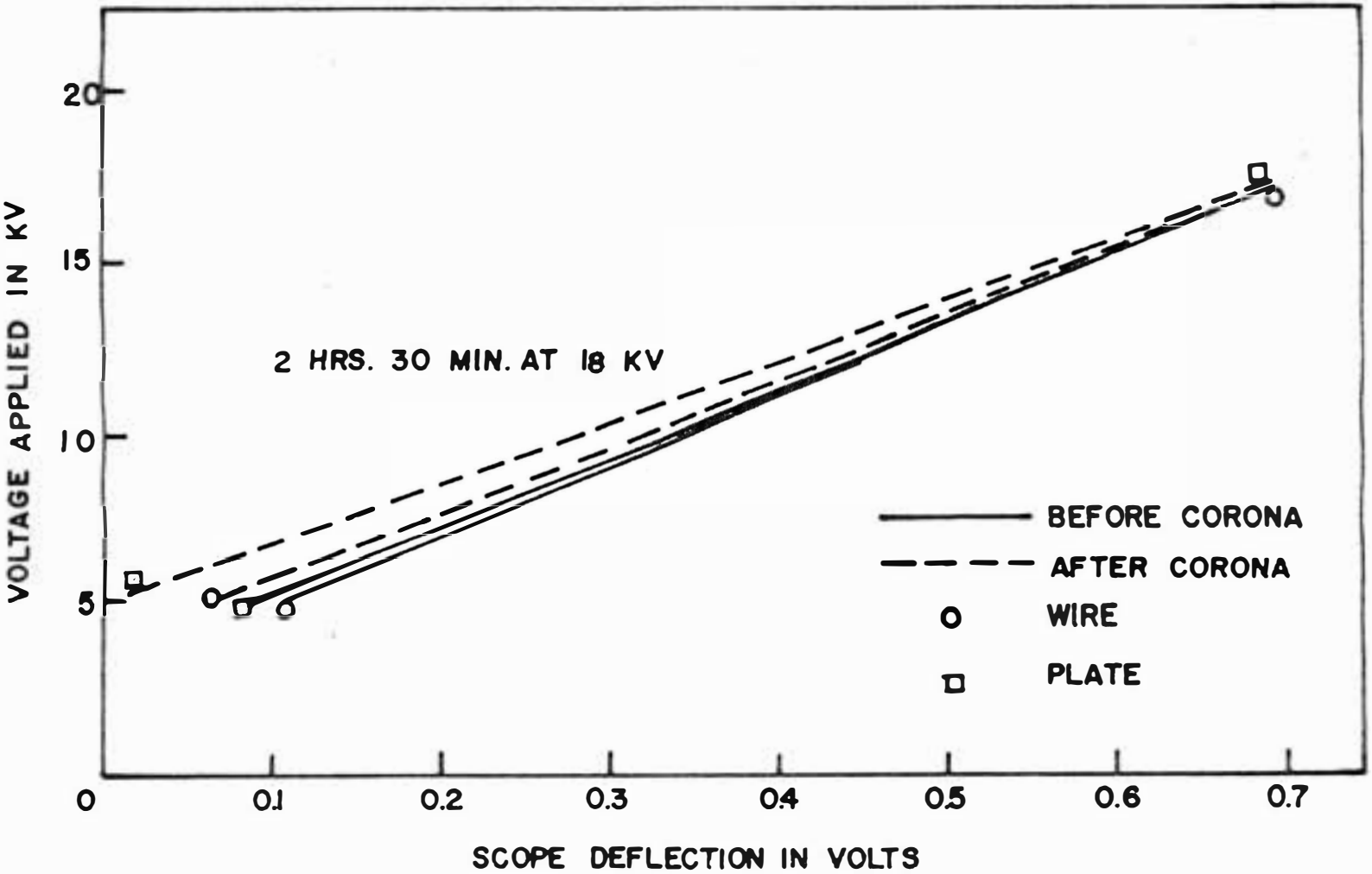


FIGURE 23. CORONA CHARACTERISTICS OF ISOPROPYL MERCAPTAN AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 60

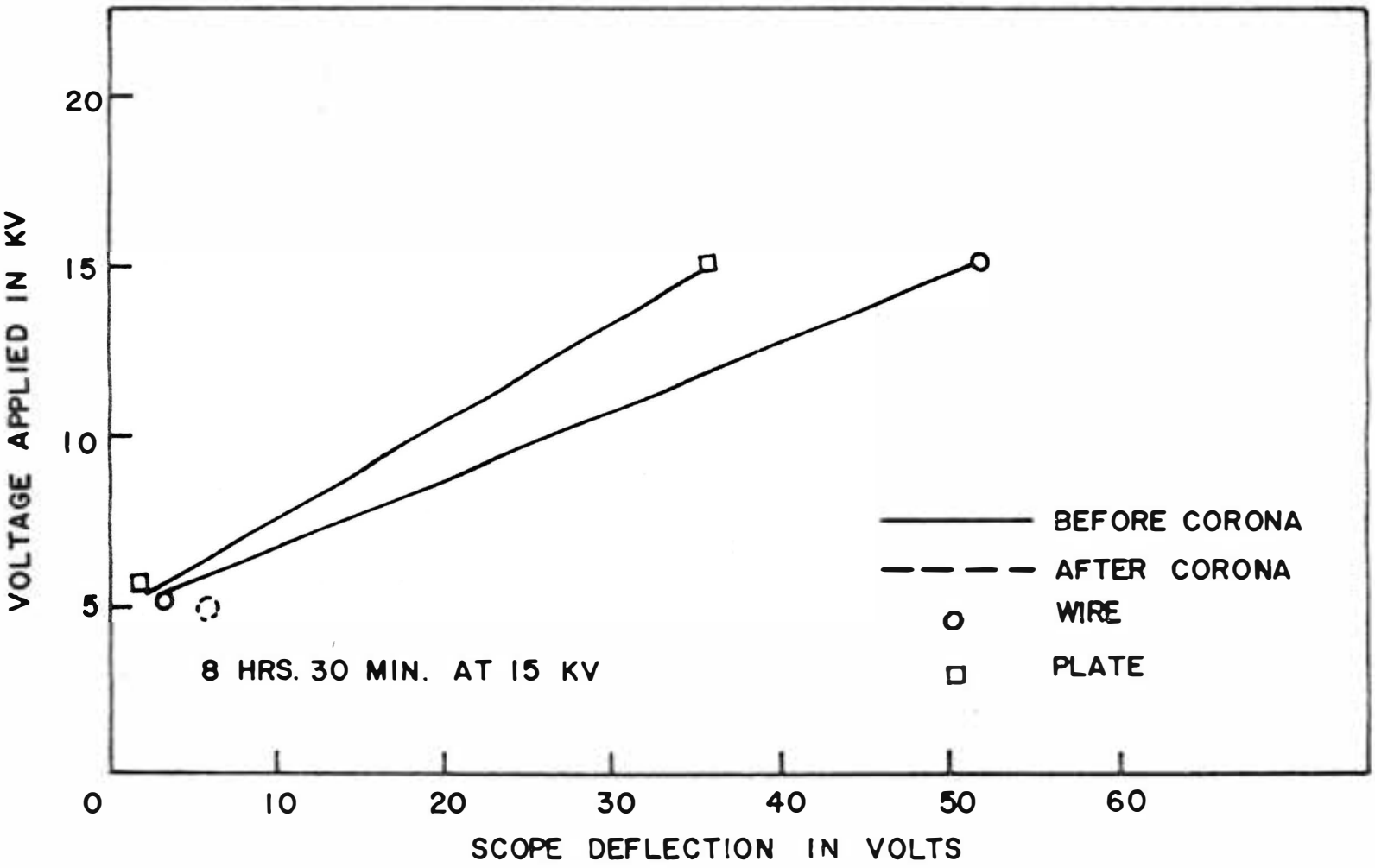


FIGURE 24. CORONA CHARACTERISTICS OF ETHYL METHYL SULFIDE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 20

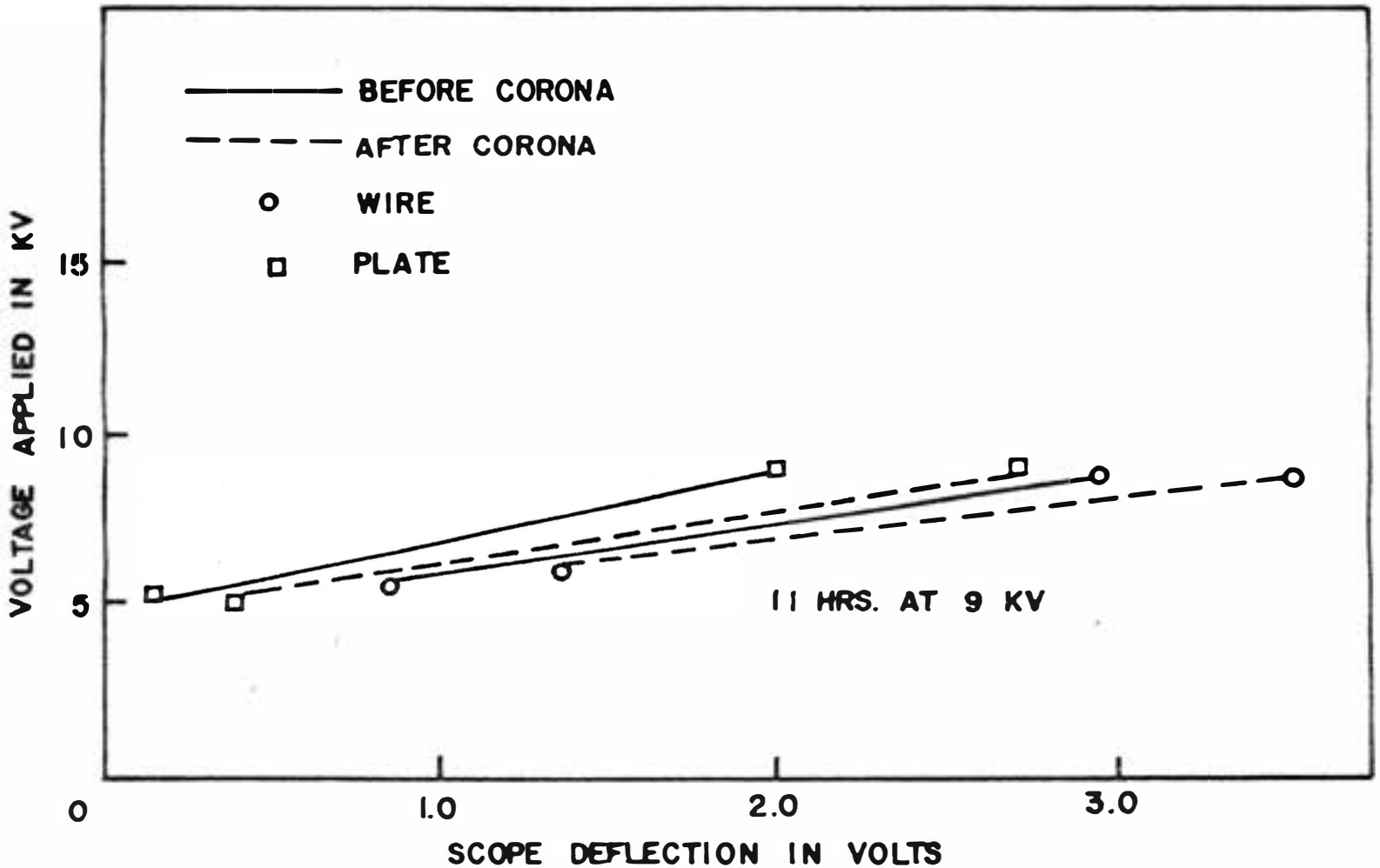


FIGURE 25. CORONA CHARACTERISTICS OF ETHYL METHYL SULFIDE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 40

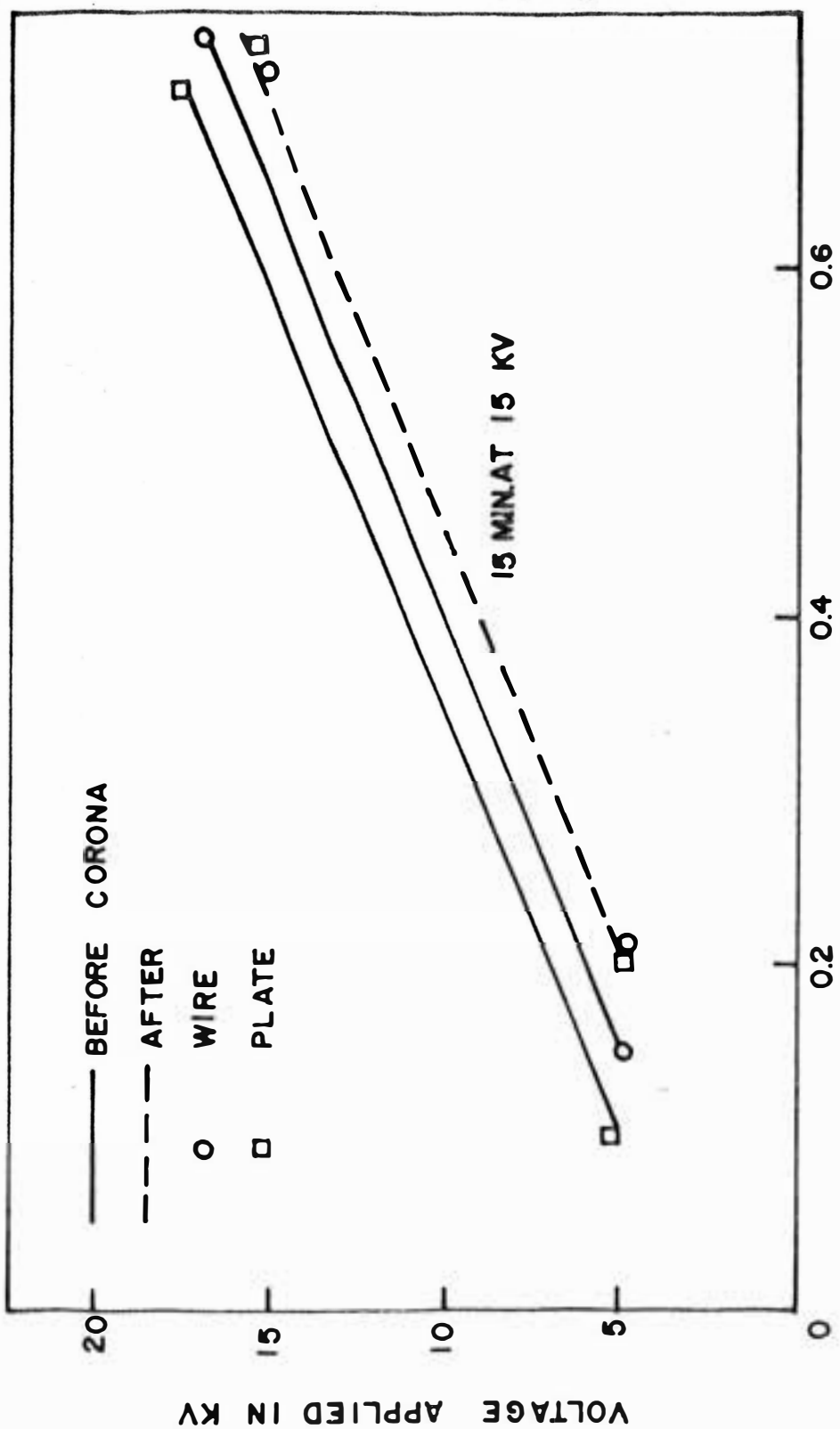


FIGURE 26. CORONA CHARACTERISTICS OF ETHYL METHYL SULFIDE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 30

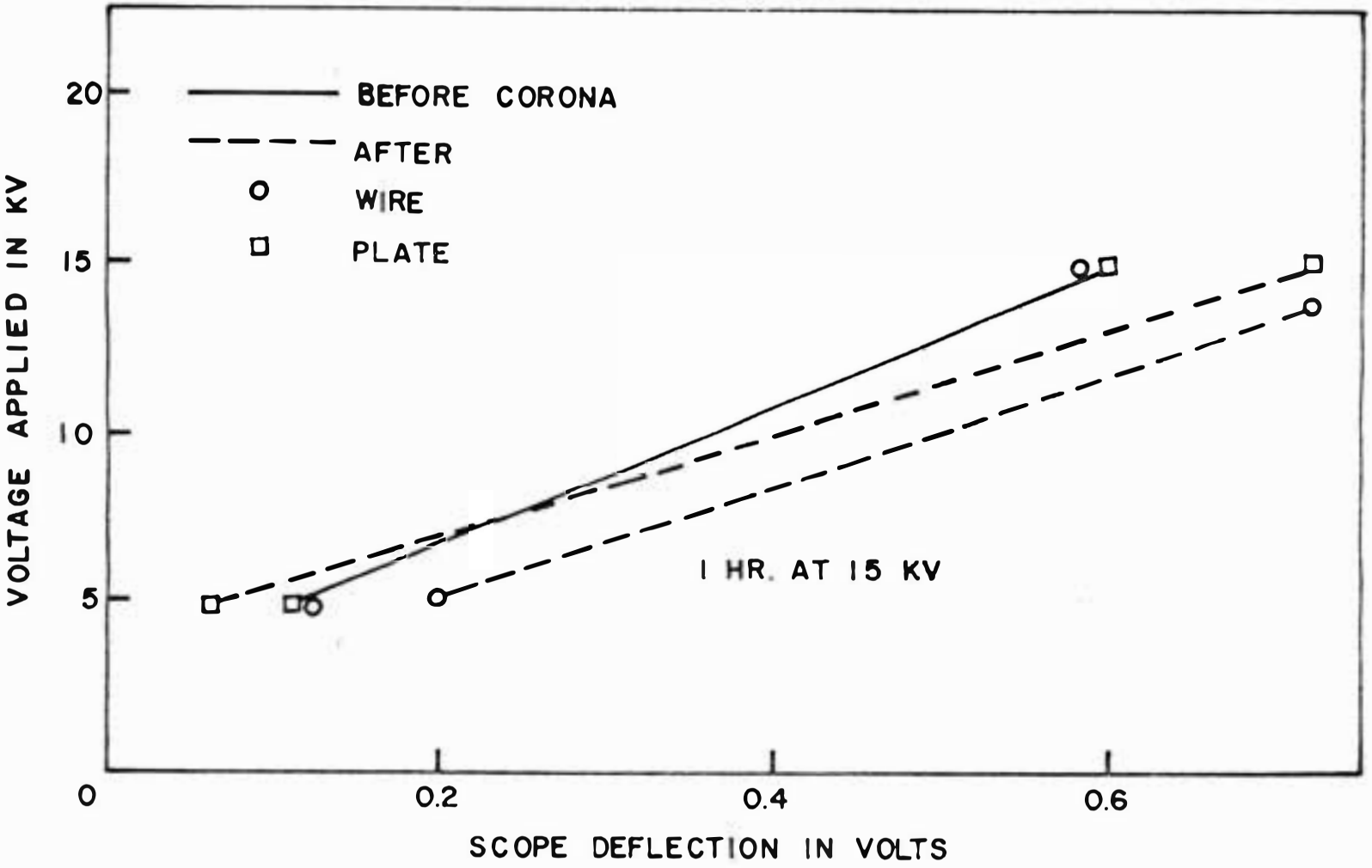


FIGURE 27. CORONA CHARACTERISTICS ETHYL METHYL SULFIDE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 30

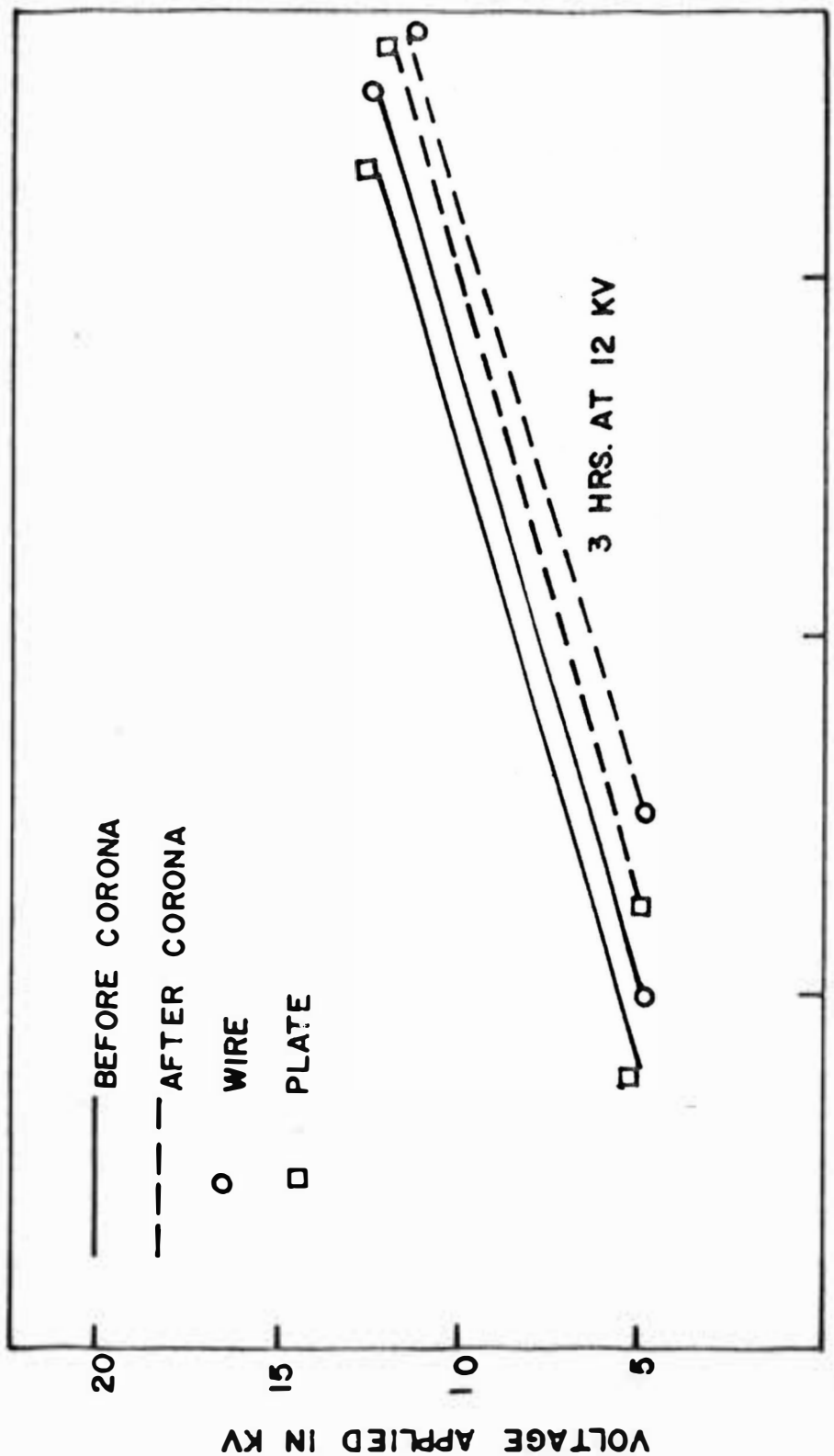


FIGURE 28. CORONA CHARACTERISTICS OF ETHYL METHYL SULFIDE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 30

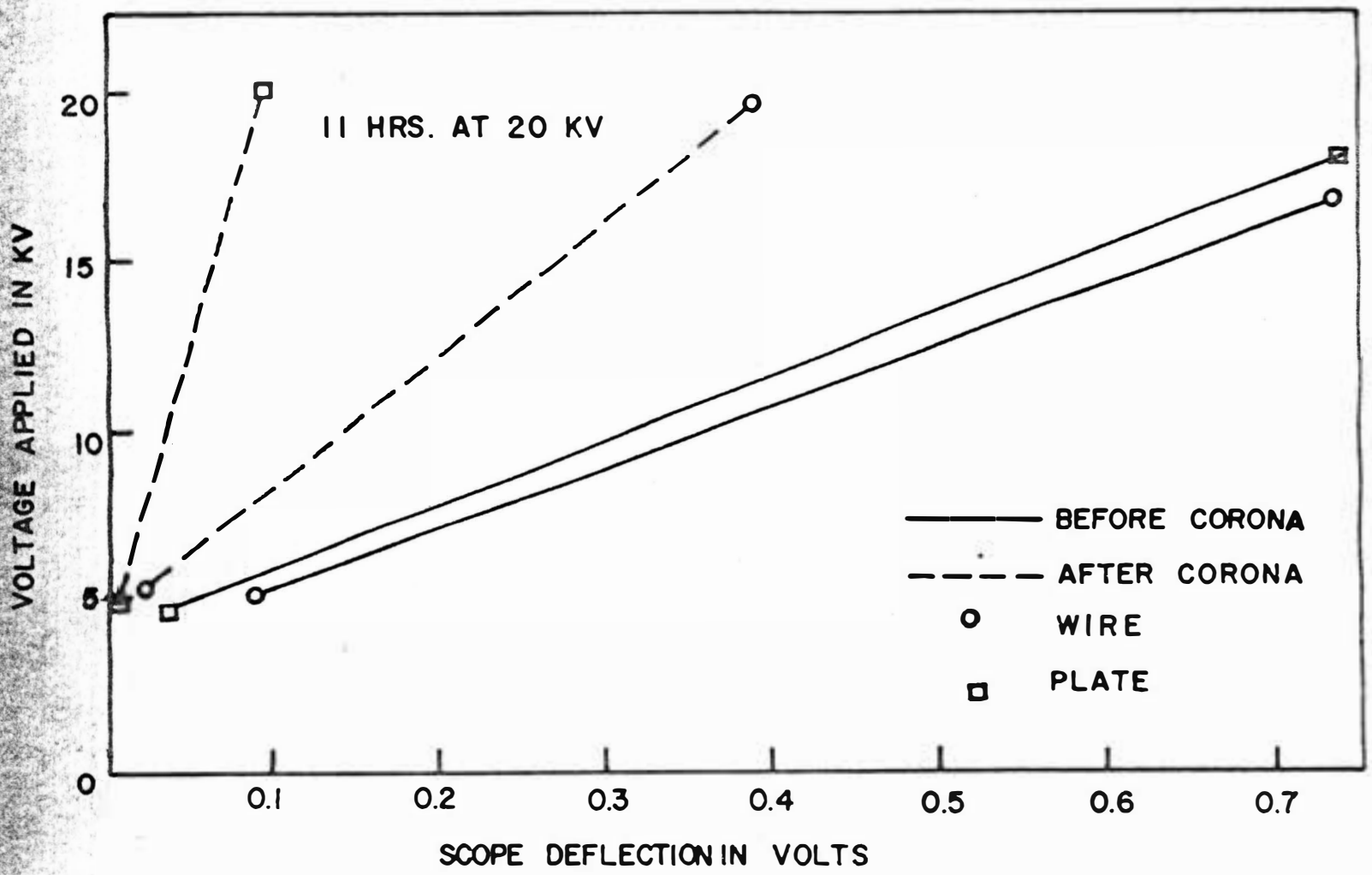


FIGURE 29. CORONA CHARACTERISTICS OF ETHYL METHYL SULFIDE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 30

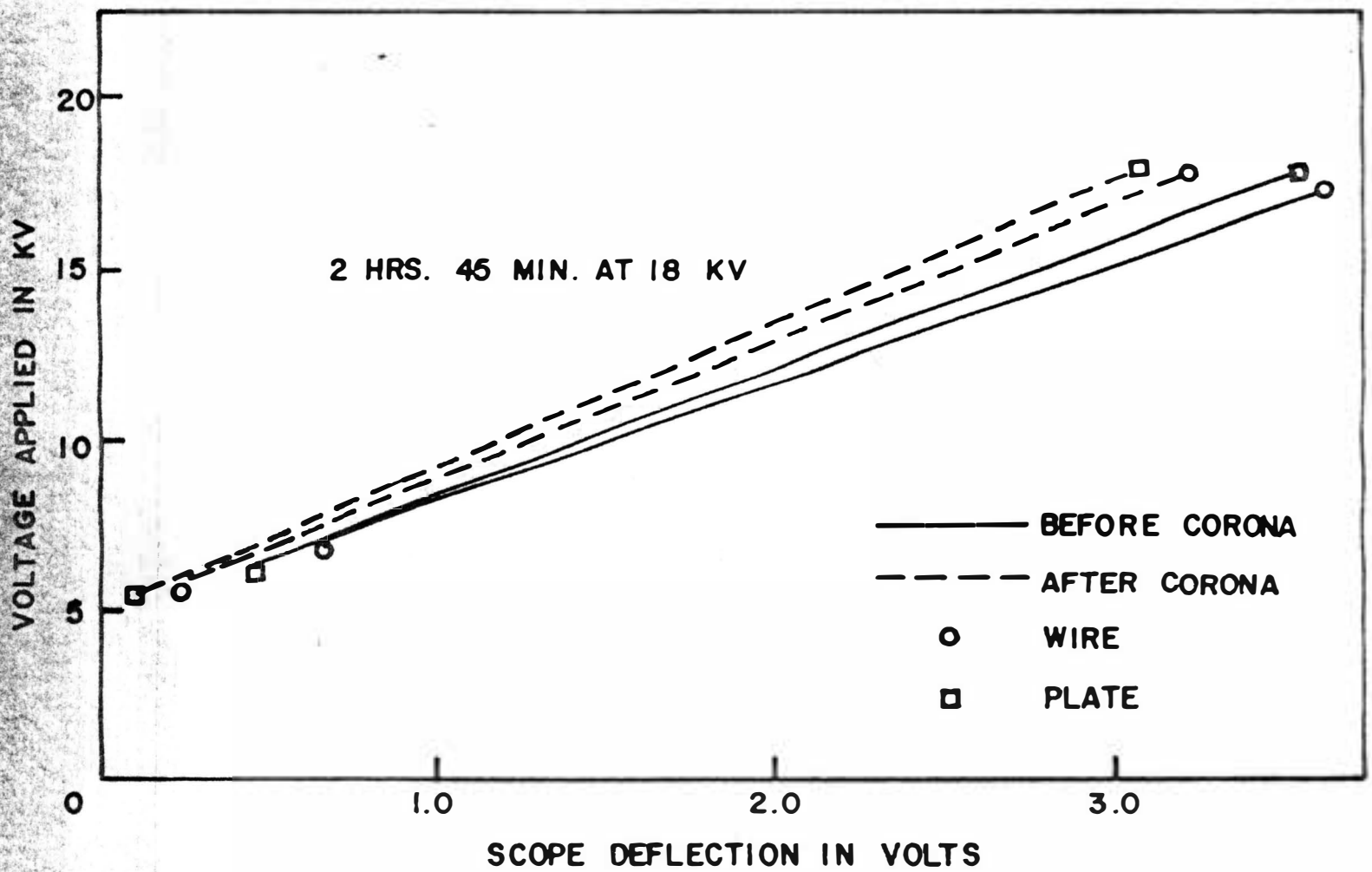


FIGURE 30. CORONA CHARACTERISTICS OF THIOPHENE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 10

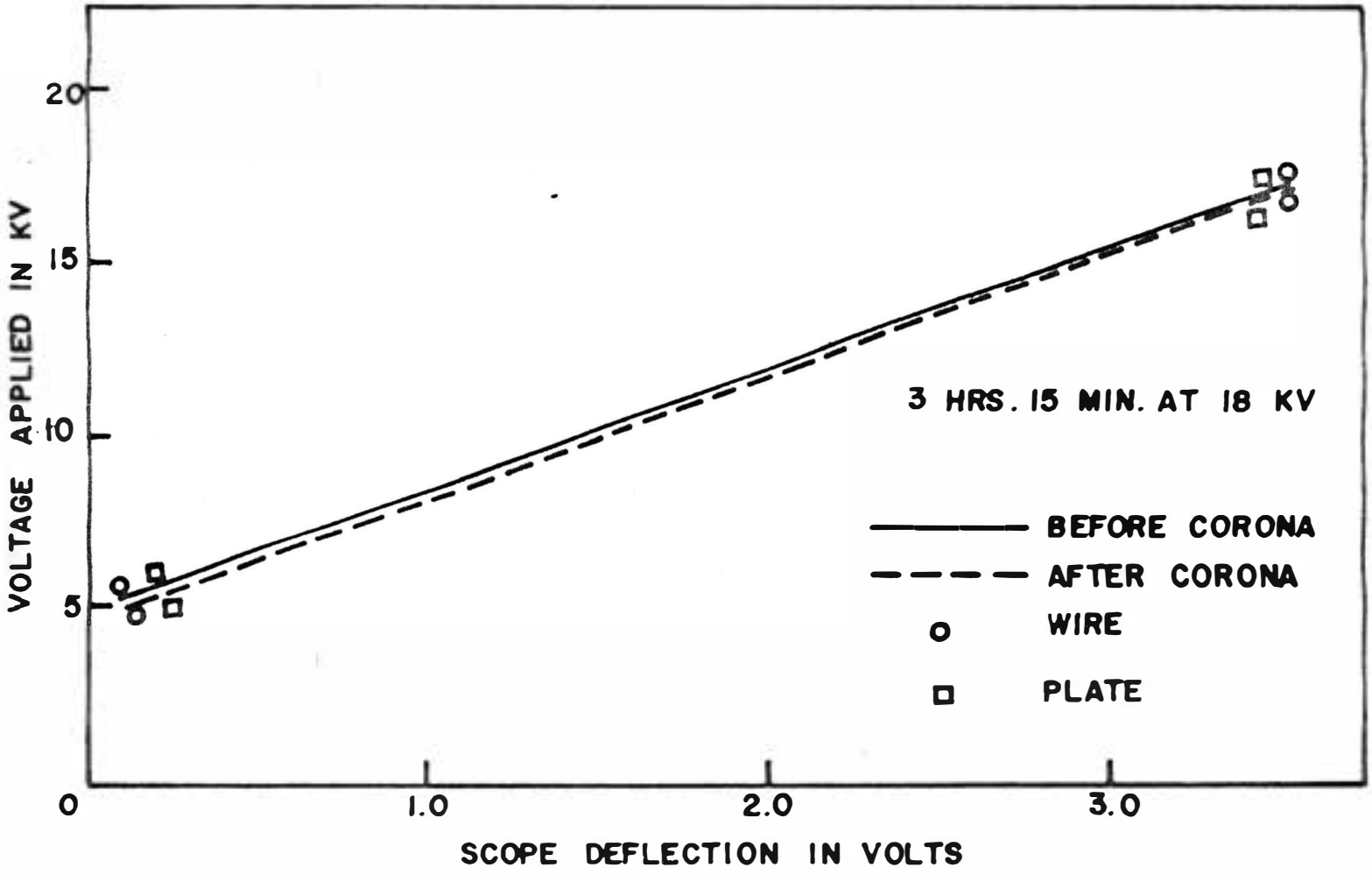


FIGURE 31. CORONA CHARACTERISTICS OF THIOPHENE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 20

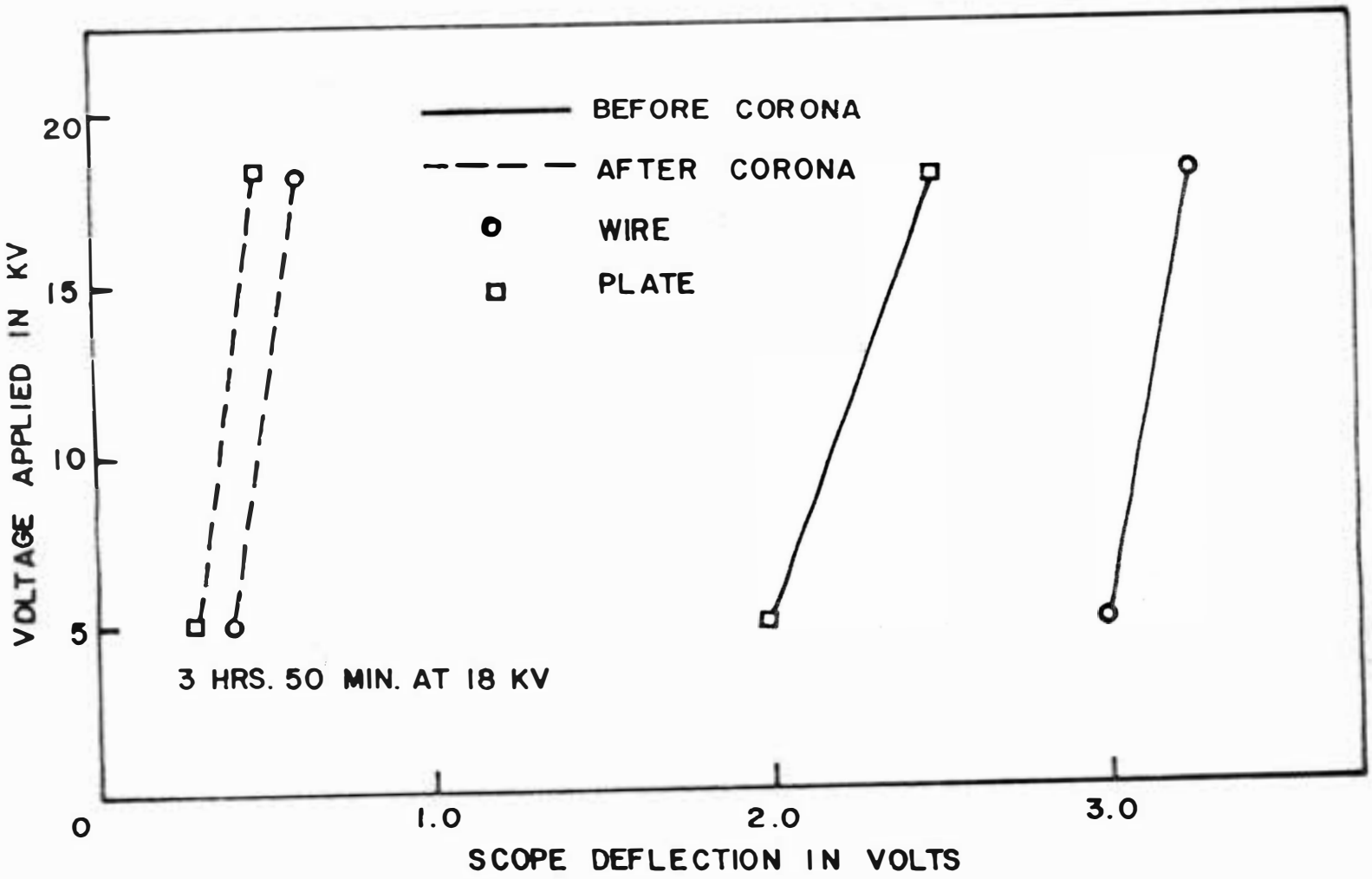


FIGURE 32. CORONA CHARACTERISTICS OF THIOPHENE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 40

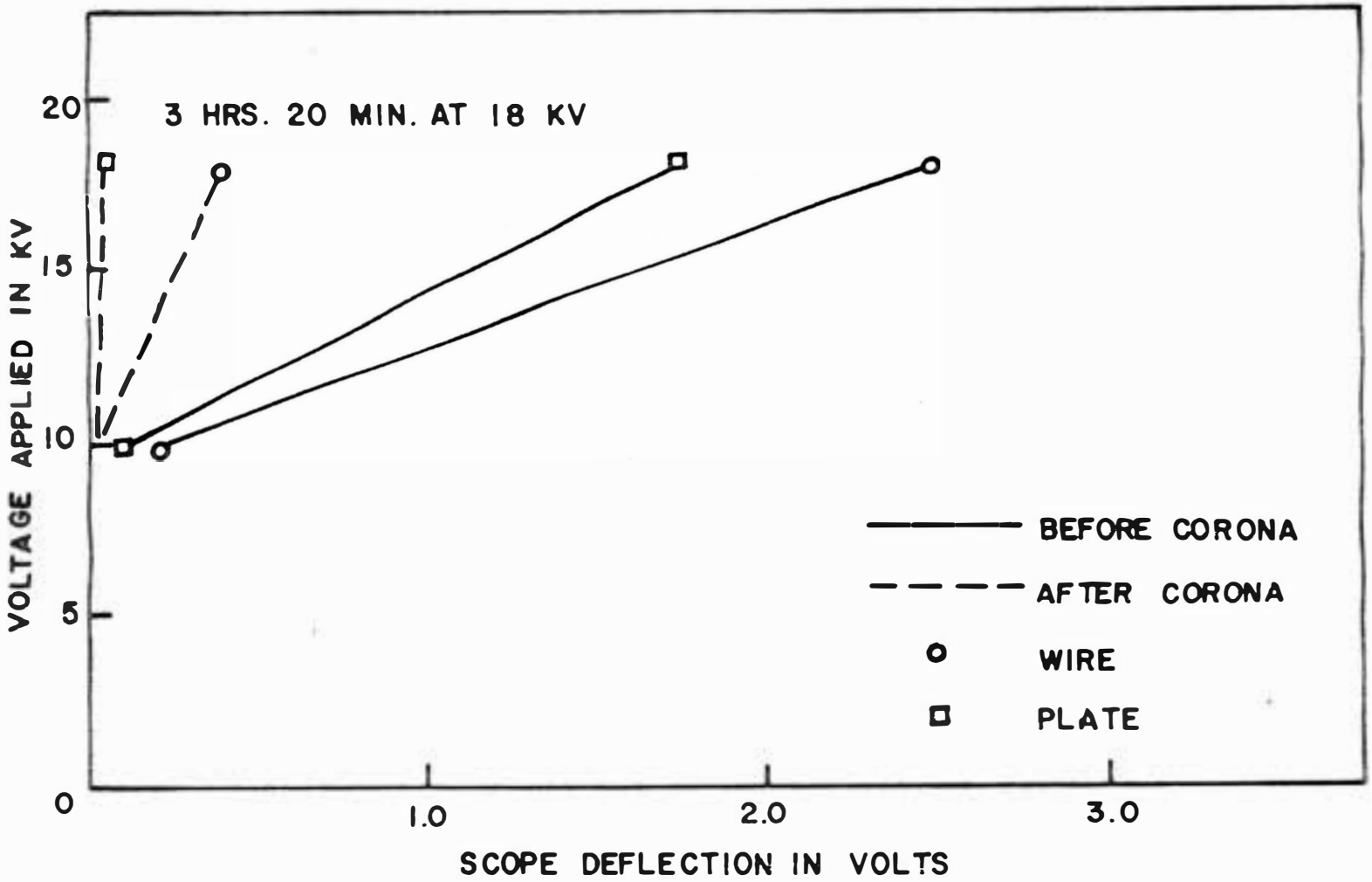


FIGURE 33. CORONA CHARACTERISTICS OF THIOPHENE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 60

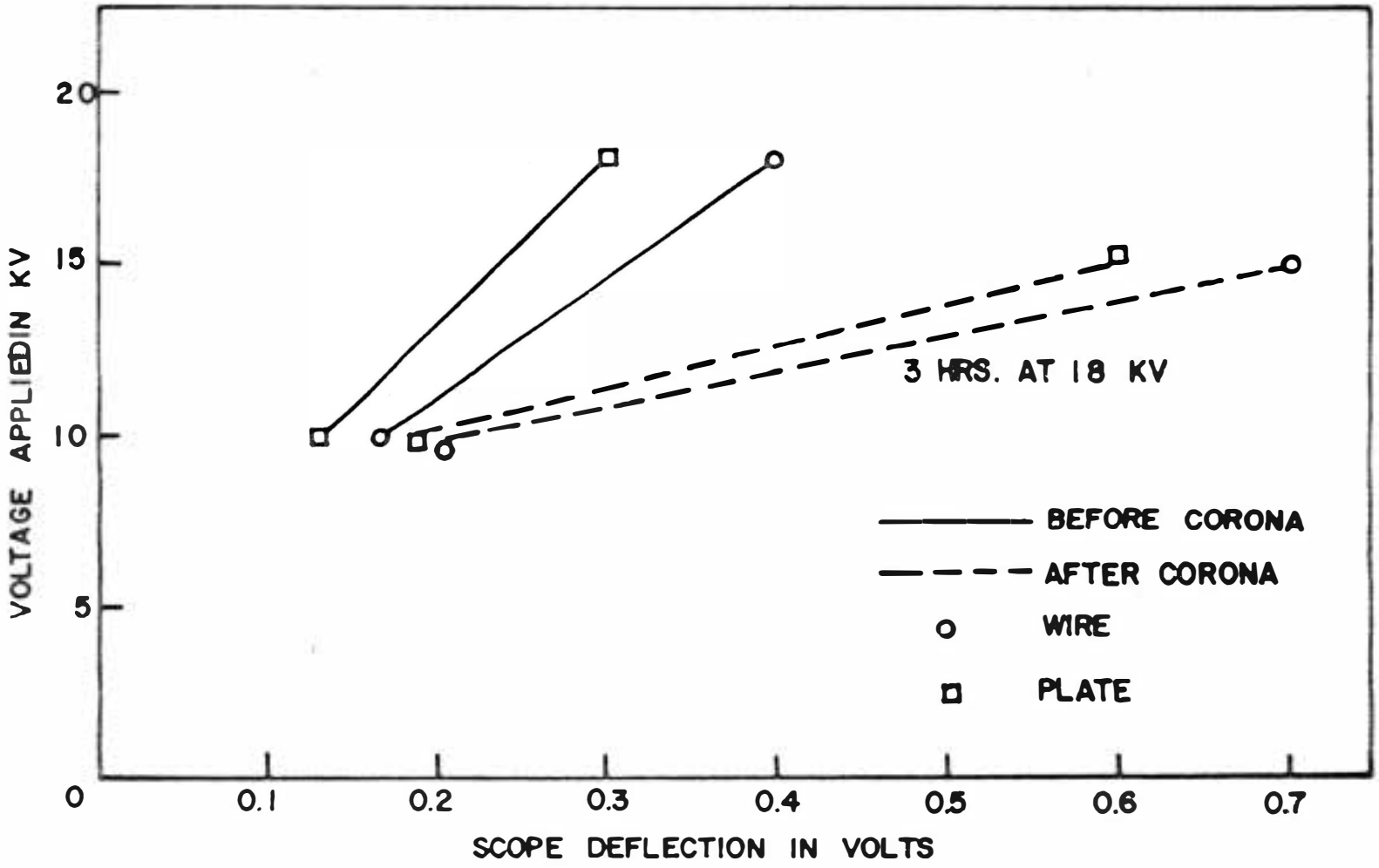


FIGURE 34. CORONA CHARACTERISTICS OF DIMETHYL DISULFIDE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 10

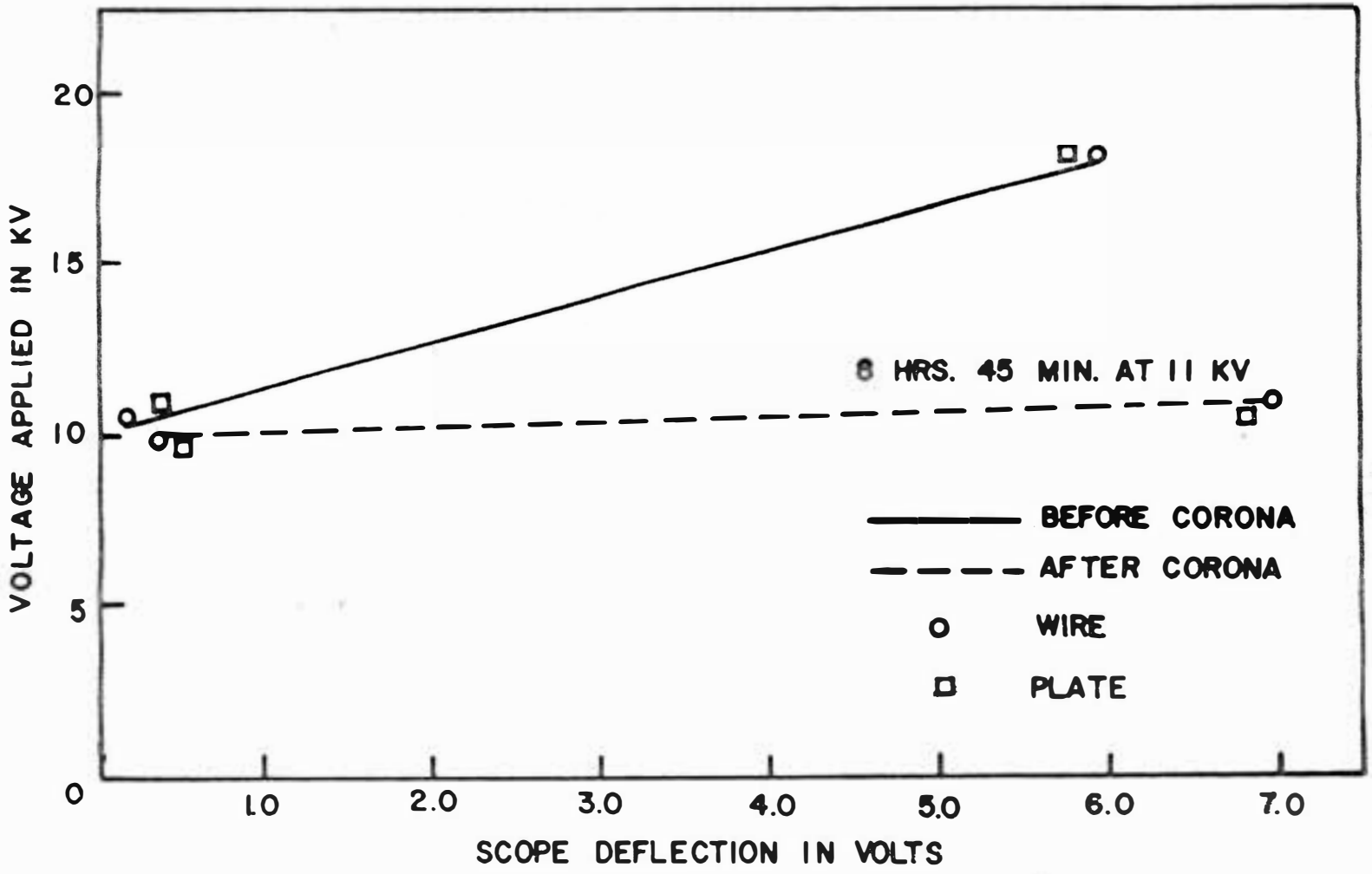


FIGURE 35. CORONA CHARACTERISTICS OF DIMETHYL DISULFIDE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 20

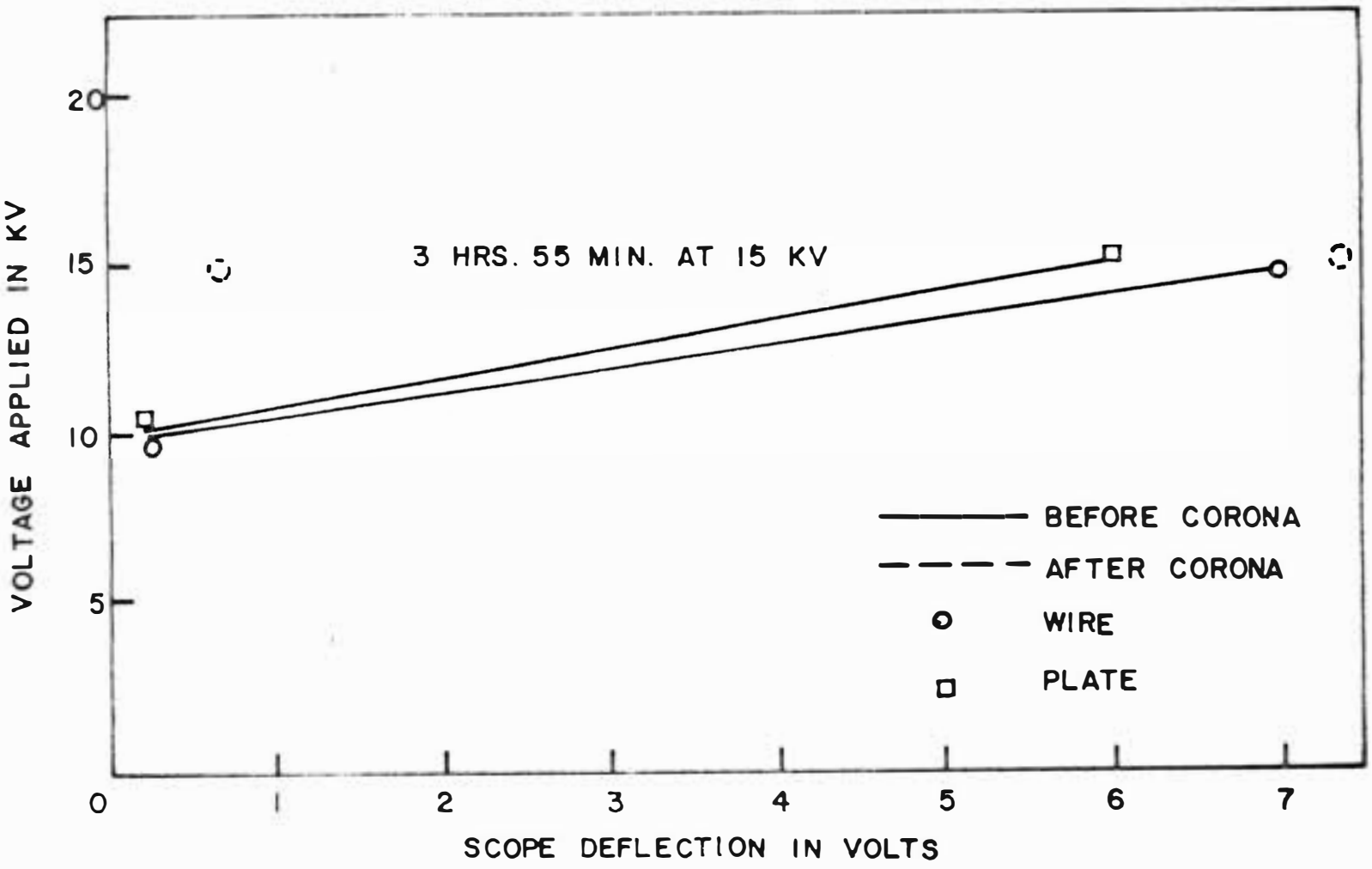


FIGURE 36. CORONA CHARACTERISTICS OF DIMETHYL DISULFIDE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 40

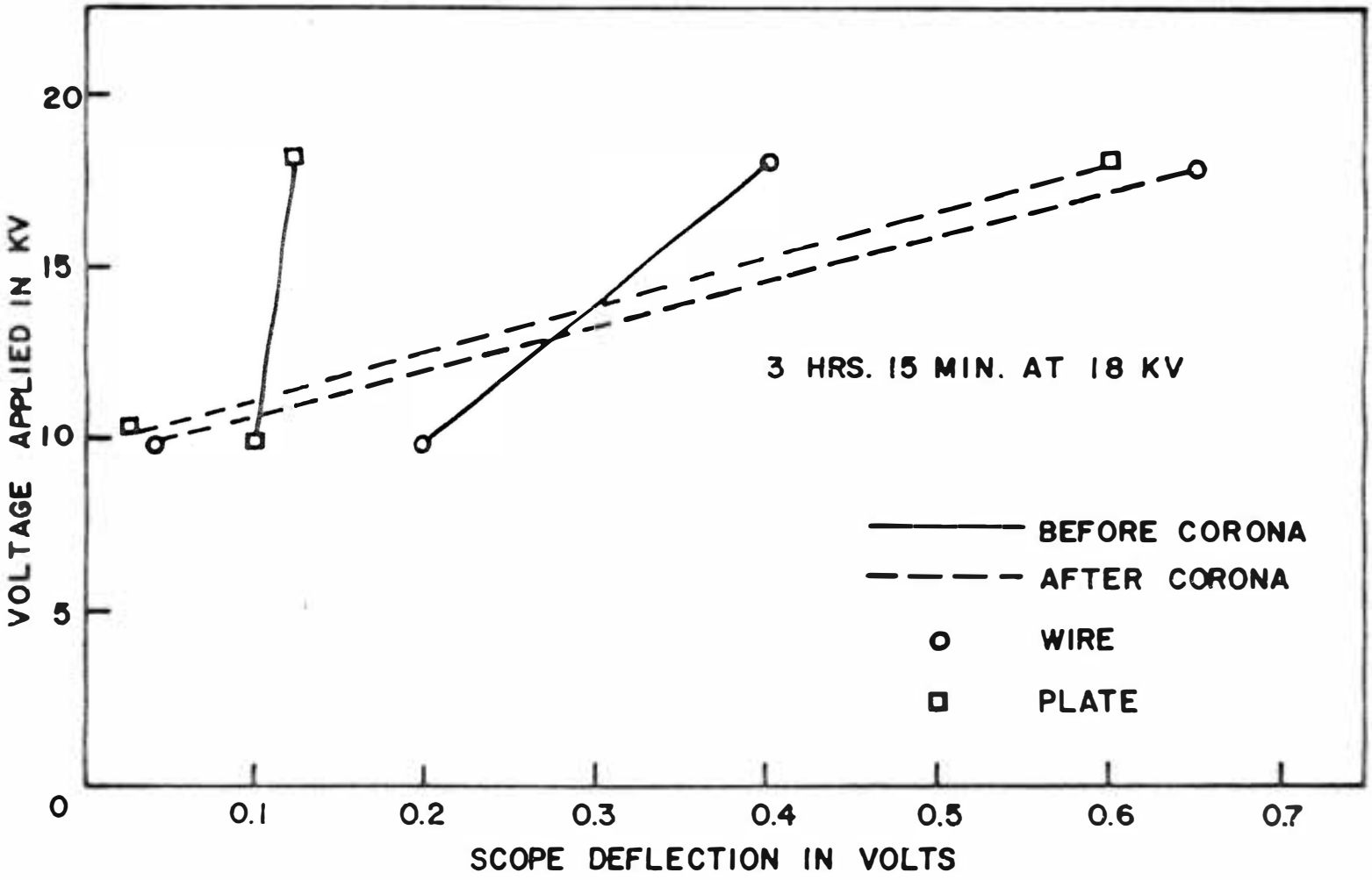
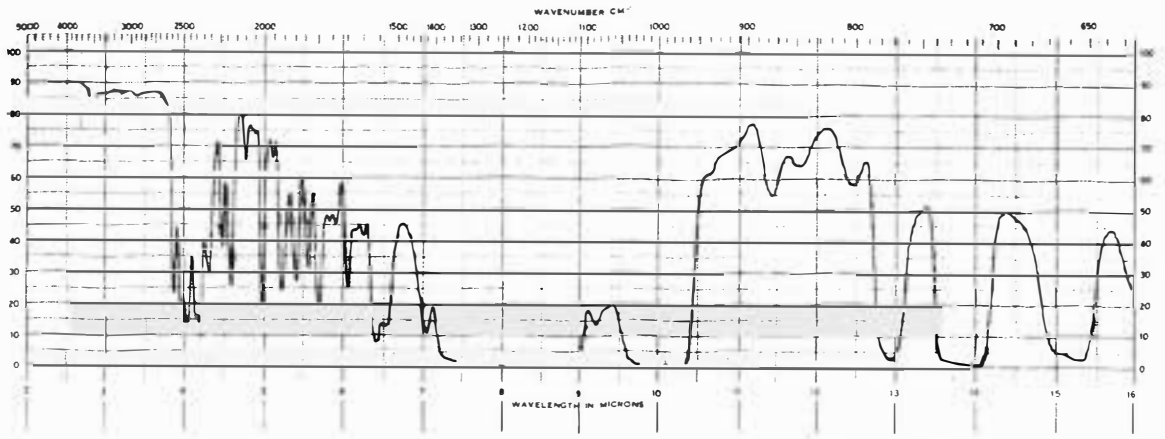
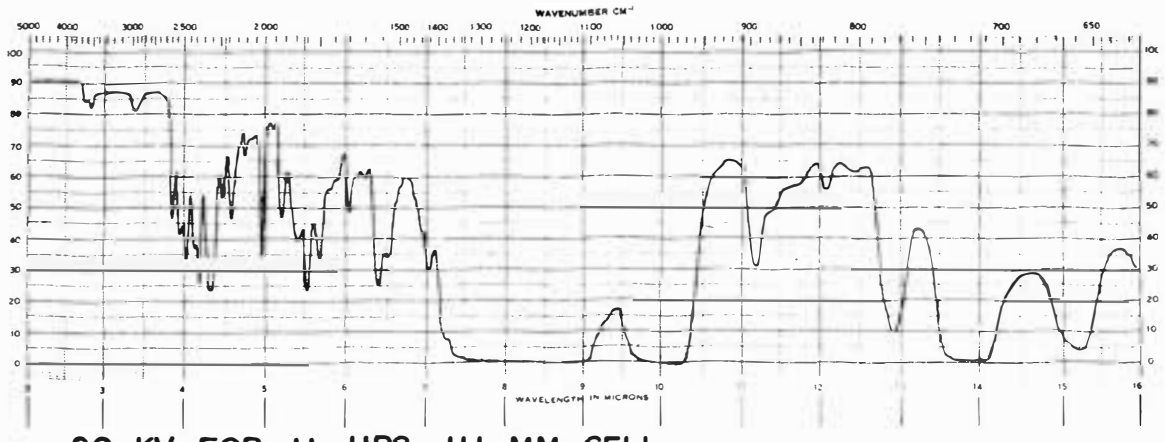


FIGURE 37. CORONA CHARACTERISTICS OF DIMETHYL DISULFIDE AND PERFLUOROPROPANE OF MOLAR RATIO 1 TO 60

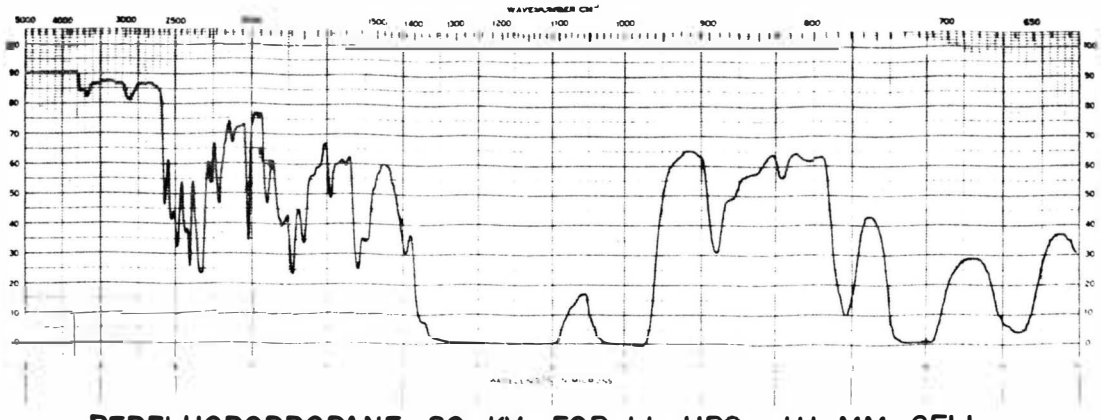


PERFLUOROPROPANE WITHOUT ADDITIVE BEFORE CORONA
111 MM CELL ATMOSPHERIC PRESSURE

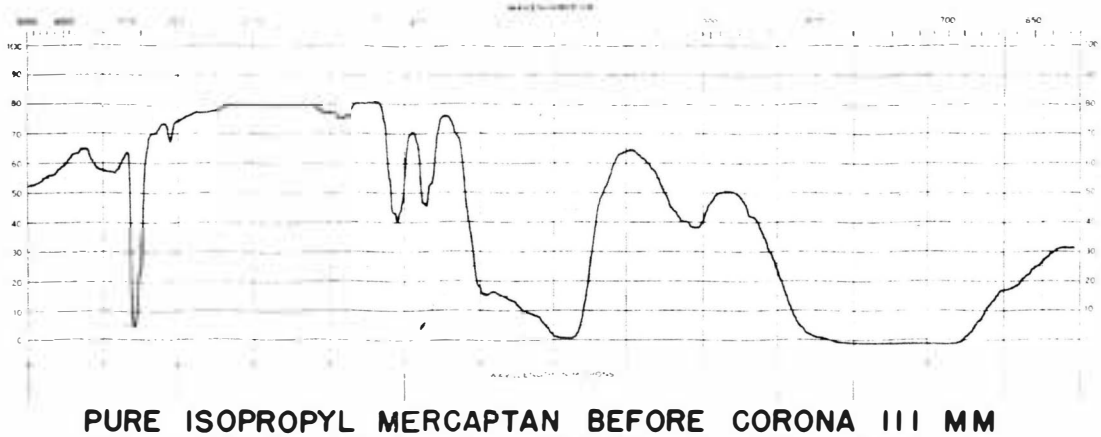


20 KV FOR 11 HRS. 111 MM CELL

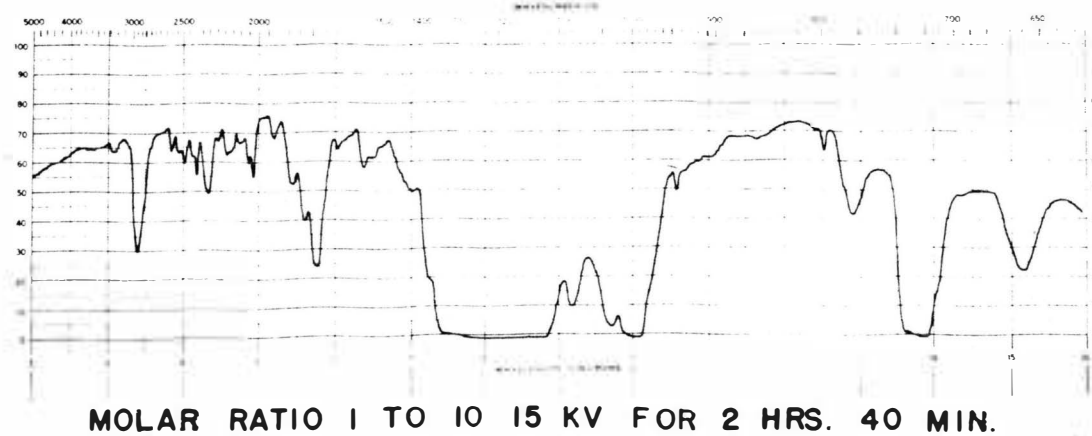
FIGURE 38. INFRARED OF PERFLUORO-PROPANE



PERFLUOROPROPANE 20 KV FOR 11 HRS. 111 MM CELL

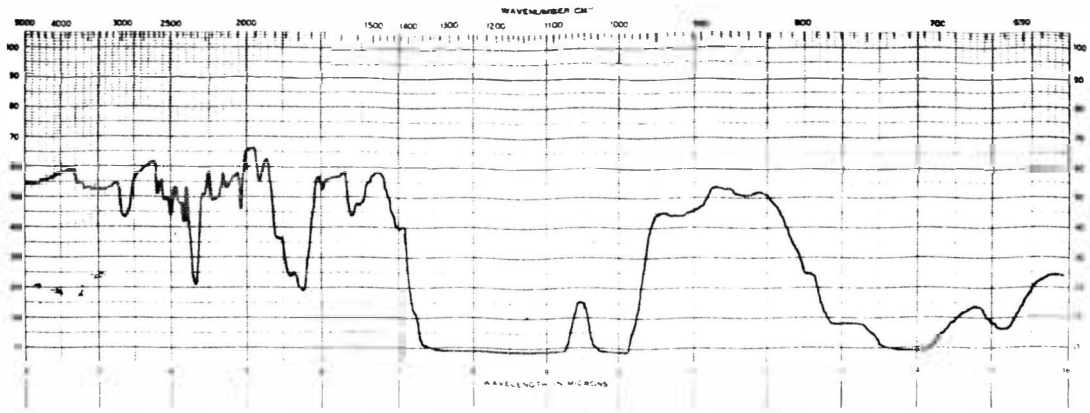


PURE ISOPROPYL MERCAPTAN BEFORE CORONA 111 MM CELL 0.5 ML LIQUID EVAPORATED TO 500 ML GAS

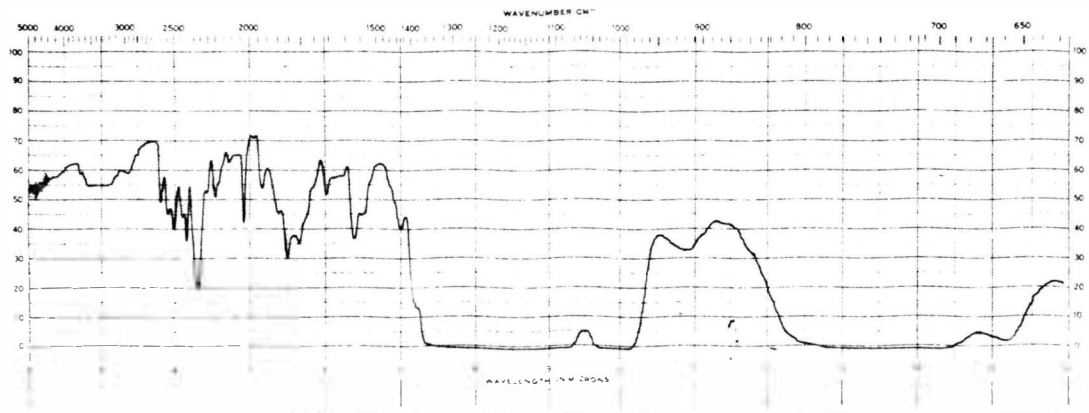


MOLAR RATIO 1 TO 10 15 KV FOR 2 HRS. 40 MIN. 112 MM CELL

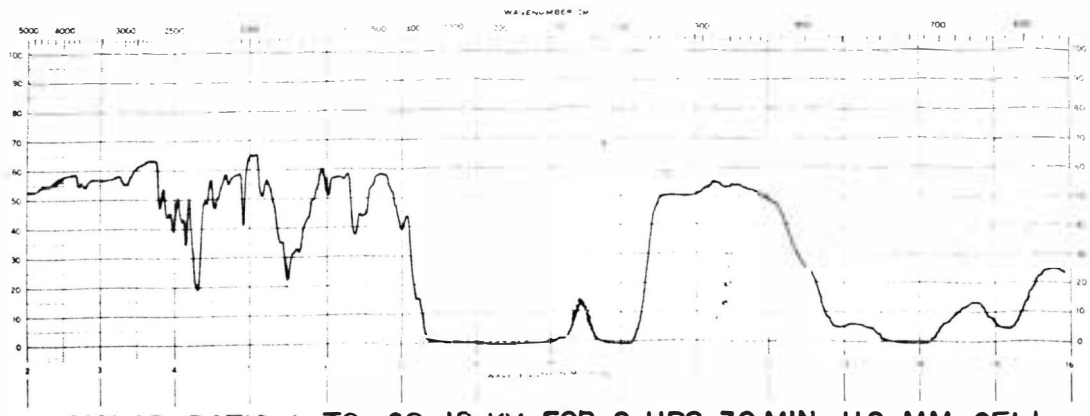
FIGURE 39. INFRARED OF ISOPROPYL MERCAPTAN AND PERFLUOROPROPANE



MOLAR RATIO 1 TO 20 15 KV FOR 3 HRS. 112 MM CELL

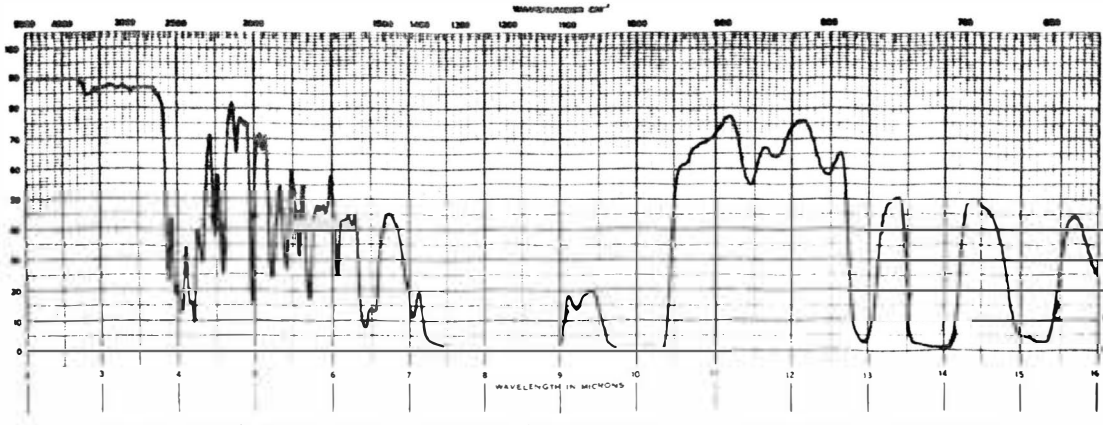


MOLAR RATIO 1 TO 40 18 KV FOR 2 HRS. 25 MIN. 111 MM CELL

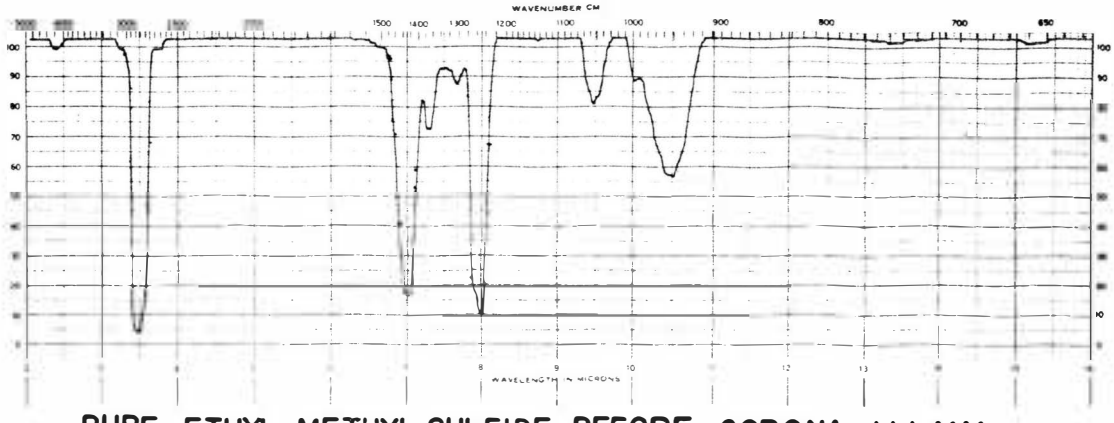


MOLAR RATIO 1 TO 60 18 KV FOR 2 HRS. 30 MIN. 112 MM CELL

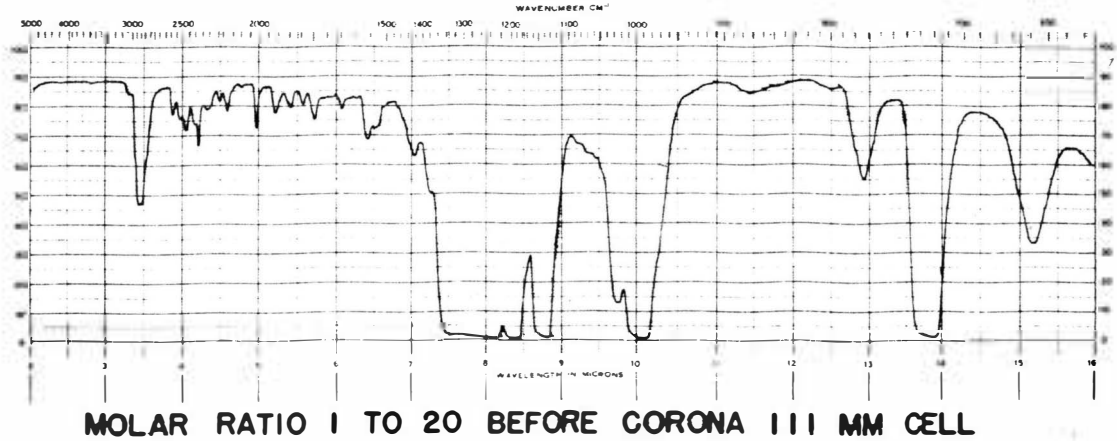
FIGURE 40. INFRARED OF ISOPROPYL MERCAPTAN AND PERFLUOROPROPANE



PERFLUOROPROPANE WITHOUT ADDITIVE BEFORE CORONA
111 MM CELL ATMOSPHERIC PRESSURE



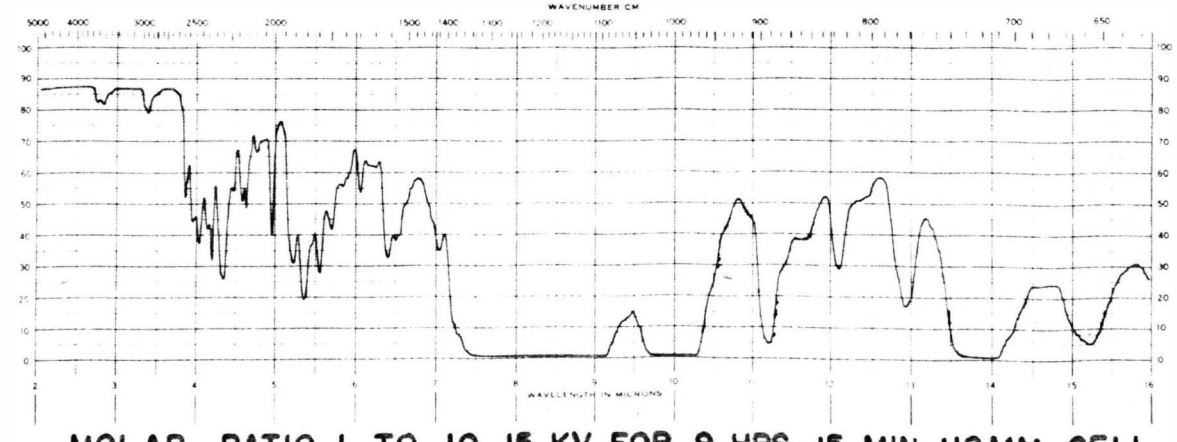
PURE ETHYL METHYL SULFIDE BEFORE CORONA 111 MM
CELL 0.5 ML LIQUID EVAPORATED TO 500 ML GAS



MOLAR RATIO 1 TO 20 BEFORE CORONA 111 MM CELL

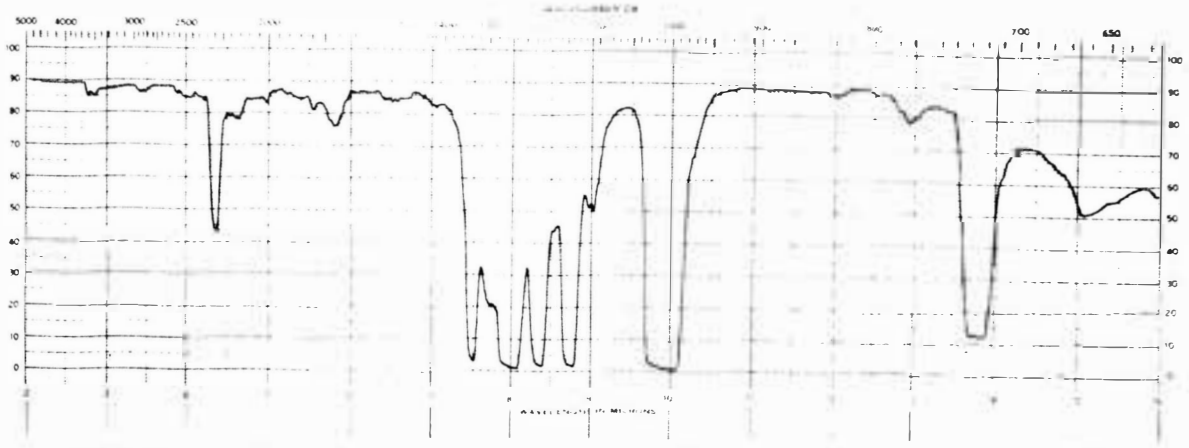
FIGURE 41. INFRARED OF ETHYL METHYL SULFIDE AND PERFLUOROPROPANE

MOLAR RATIO 1 TO 5 18 KV FOR 12 HRS. 112 MM CELL

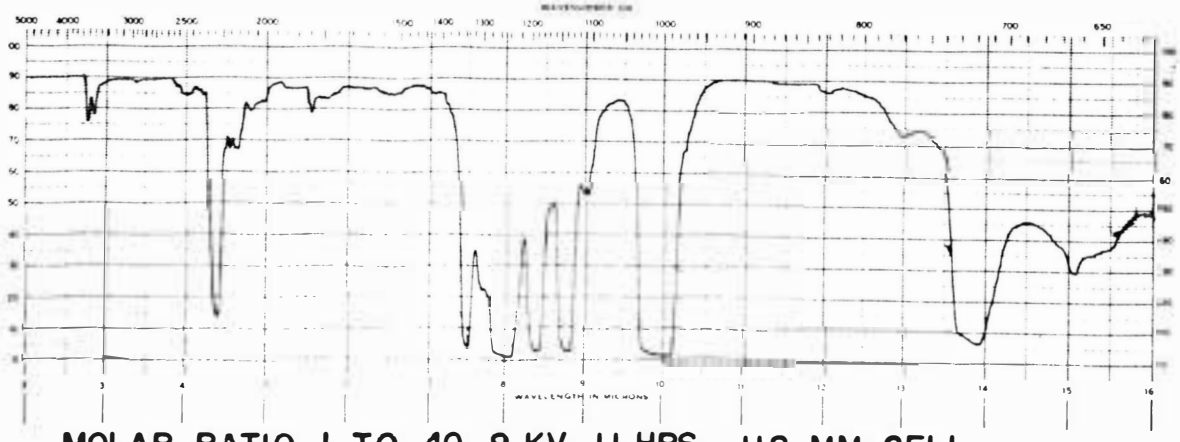


MOLAR RATIO 1 TO 10 15 KV FOR 9 HRS. 15 MIN. 112MM CELL

FIGURE 42. INFRARED OF ETHYL METHYL SULFIDE AND PERFLUOROPROPANE

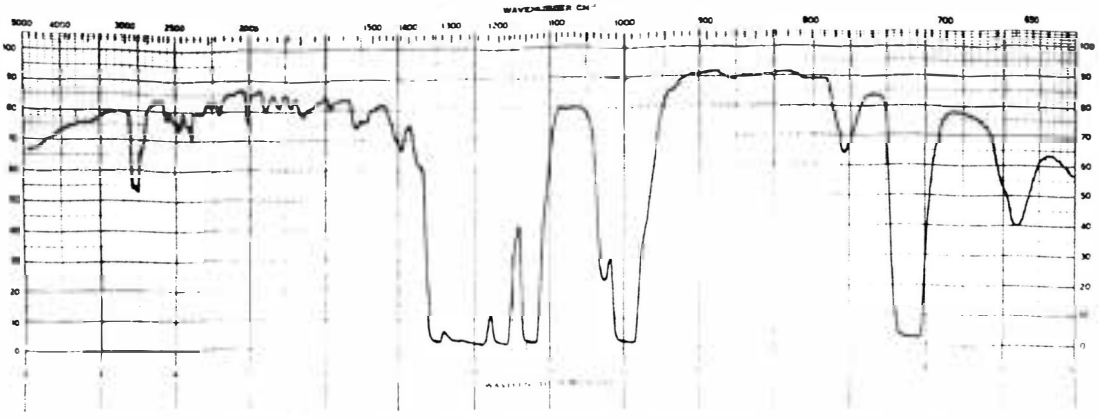


MOLAR RATIO 1 TO 20 15 KV 8 HRS. 30 MIN. 112 MM CELL

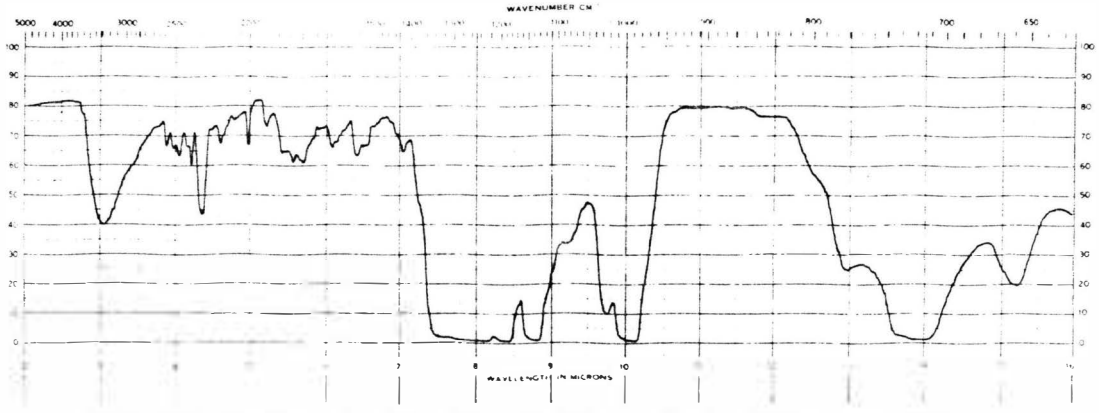


MOLAR RATIO 1 TO 40 9 KV 11 HRS. 112 MM CELL

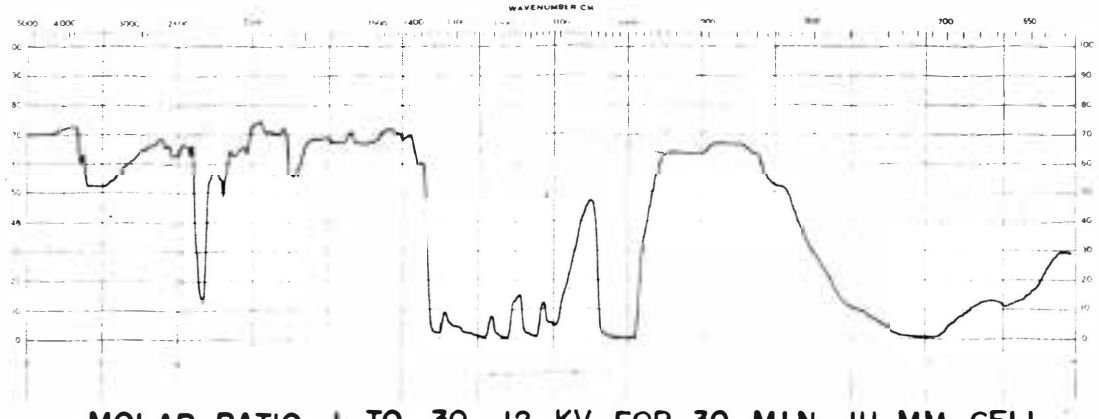
FIGURE 43. INFRARED OF ETHYL METHYL SULFIDE AND PERFLUOROPROPANE



MOLAR RATIO 1 TO 30 BEFORE CORONA 111 MM CELL

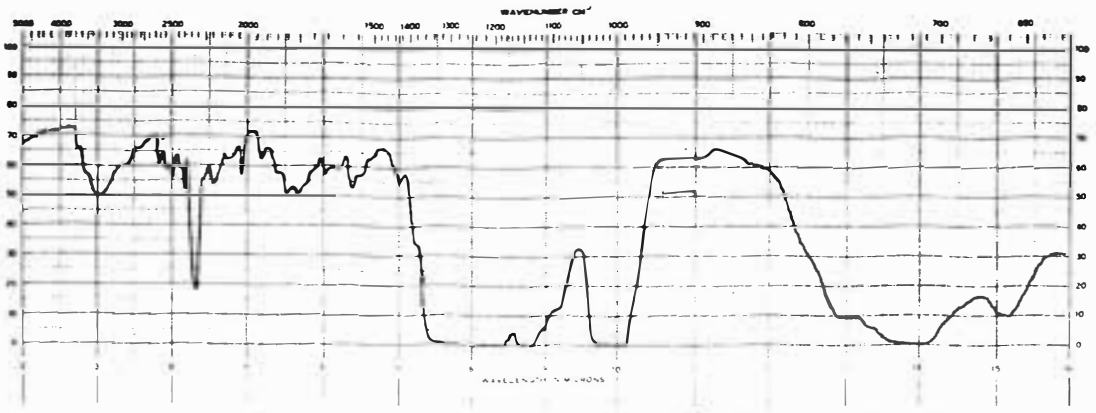


MOLAR RATIO 1 TO 30 15 KV FOR 15 MIN. 112 MM CELL

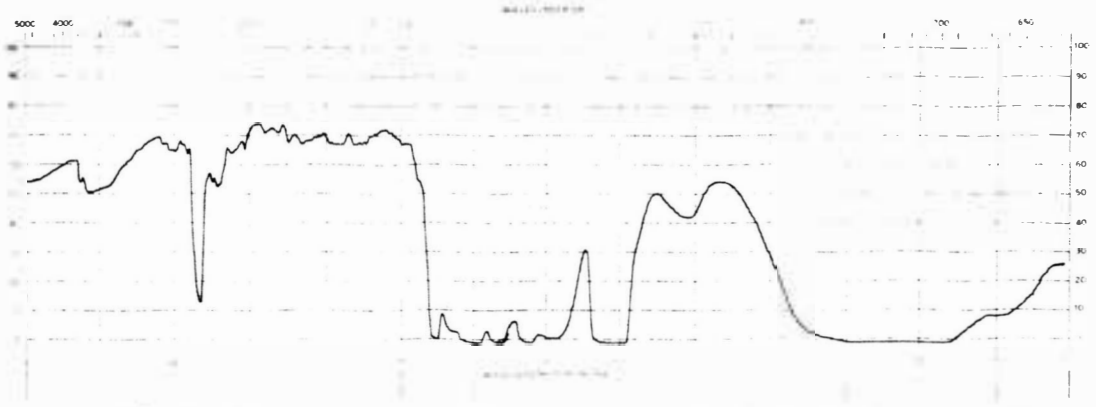


MOLAR RATIO 1 TO 30 12 KV FOR 30 MIN. 111 MM CELL

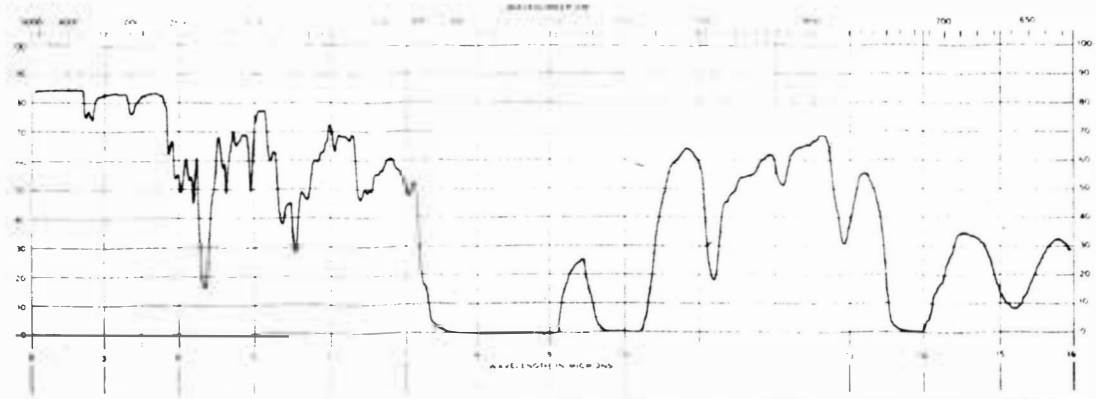
FIGURE 44. INFRARED OF ETHYL METHYL SULFIDE AND PERFLUOROPROPANE



MOLAR RATIO 1 TO 30 15 KV FOR 1 HR. 111 MM CELL

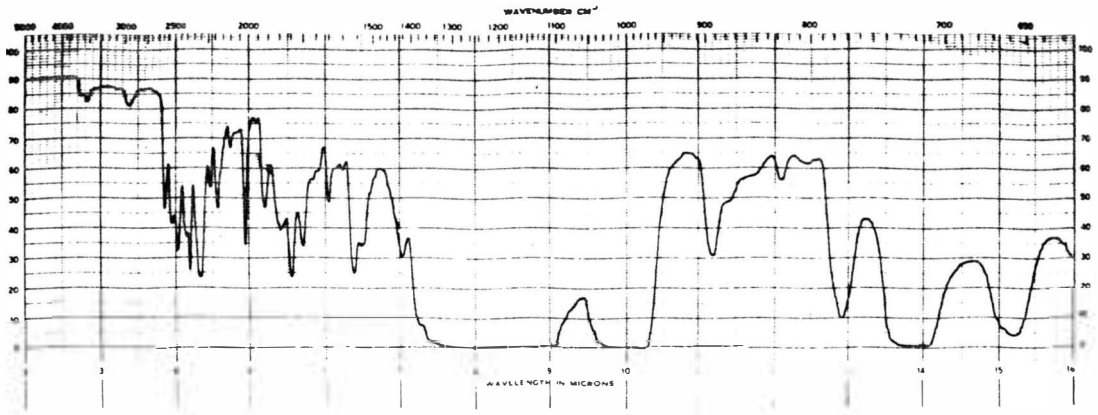


MOLAR RATIO 1 TO 30 12 KV FOR 3 HRS. 111 MM CELL

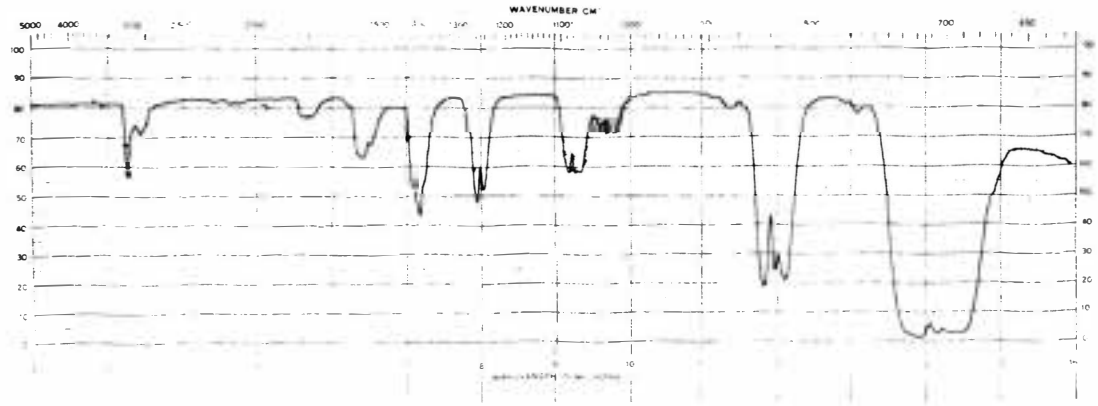


MOLAR RATIO 1 TO 30 18 KV FOR 11 HRS. 112 MM CELL

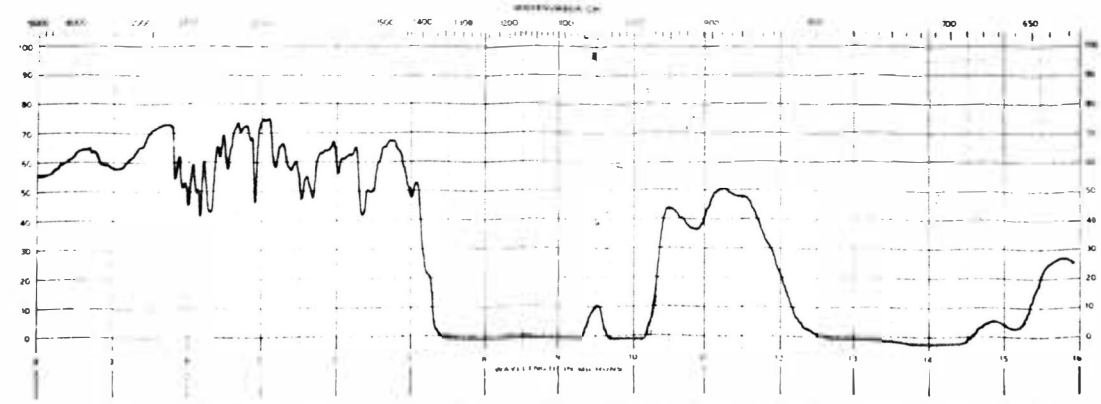
FIGURE 45. INFRARED OF ETHYL METHYL SULFIDE AND PERFLUOROPROPANE



PERFLUOROPROPANE 20 KV FOR 11 HRS. 111 MM CELL

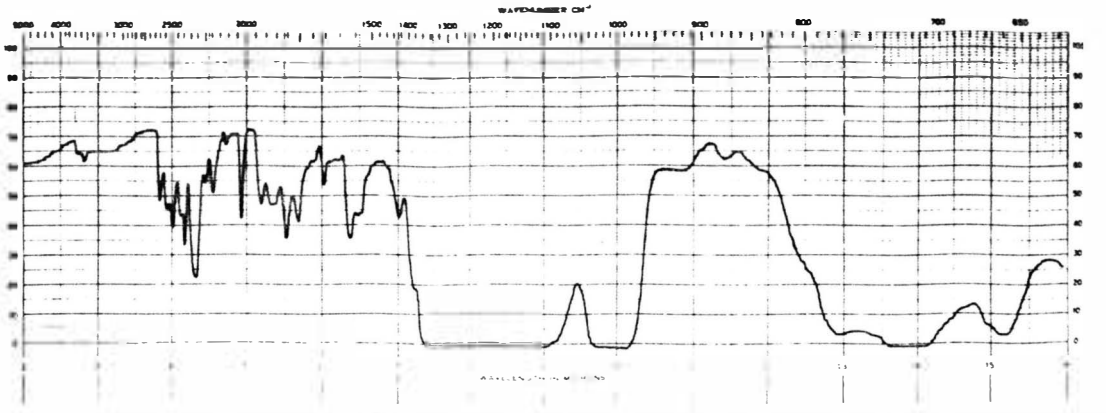


PURE THIOPHENE BEFORE CORONA 112 MM CELL 0.5 ML LIQUID EVAPORATED TO 500 ML GAS



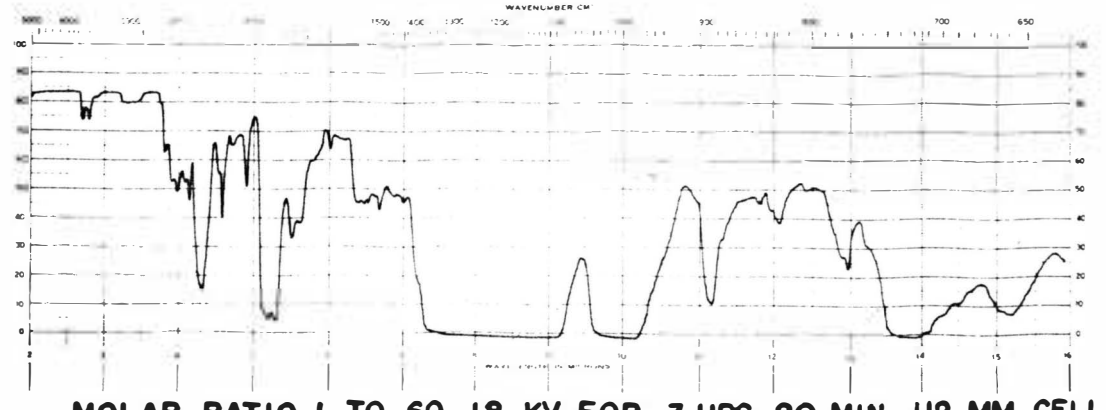
MOLAR RATIO 1 TO 10 18 KV FOR 2 HRS. 45 MIN 111 MM CELL

FIGURE 46. INFRARED OF THIOPHENE AND PERFLUOROPROPANE



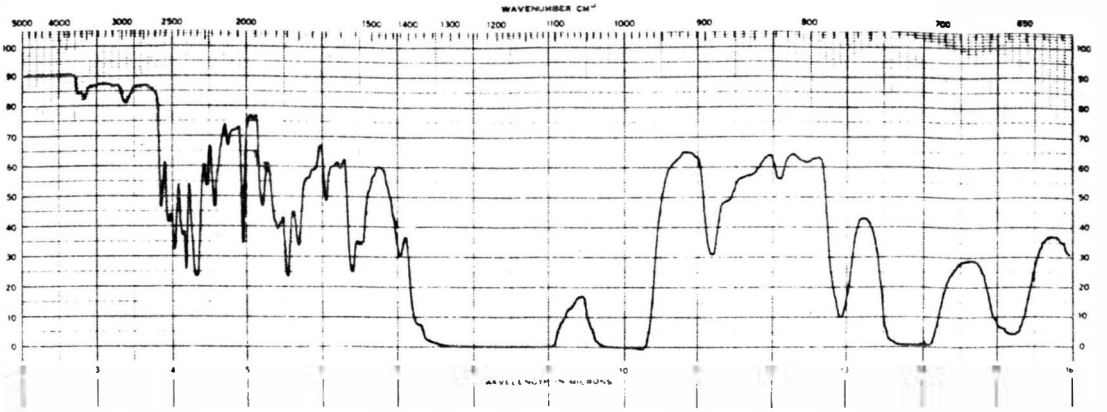
MOLAR RATIO 1 TO 20 18 KV FOR 3 HRS. 15 MIN. 112 MM CELL

MOLAR RATIO 1 TO 40 18 KV FOR 3 HRS. 50 MIN. 111 MM CELL

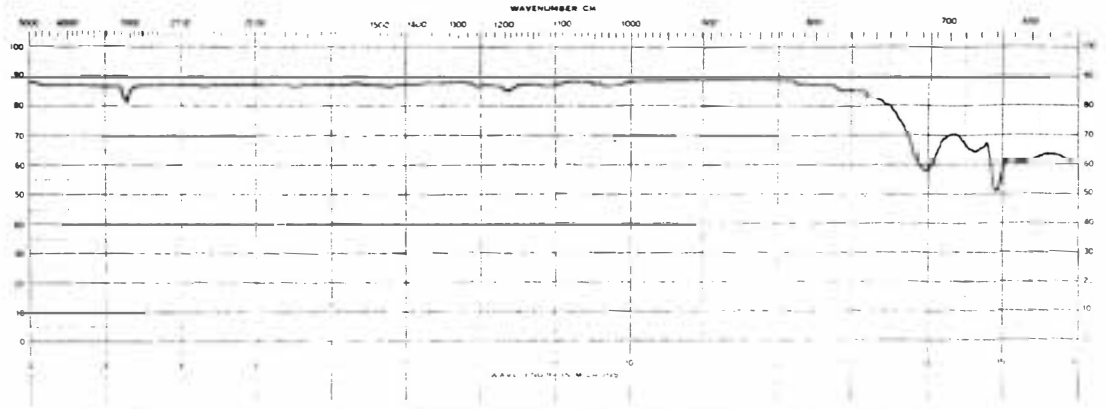


MOLAR RATIO 1 TO 60 18 KV FOR 3 HRS. 20 MIN. 112 MM CELL

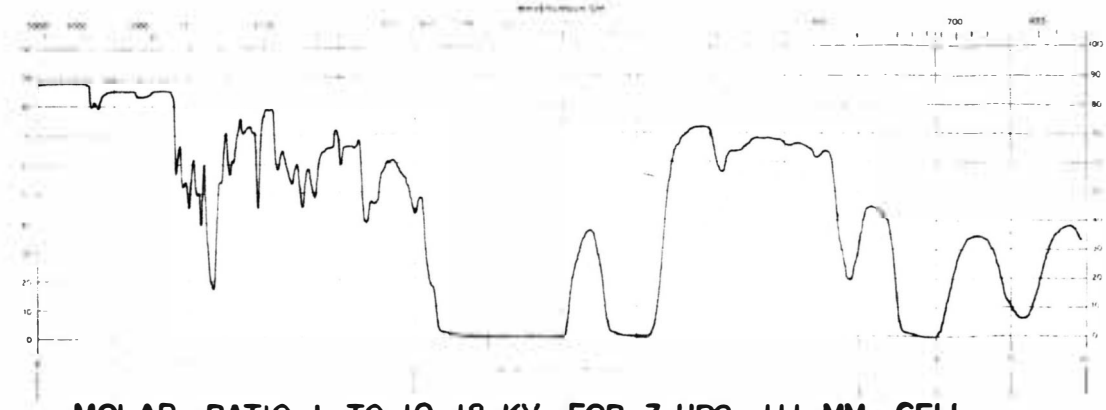
FIGURE 47. INFRARED OF THIOPHENE AND PERFLUOROPROPANE



PERFLUOROPROPANE 20 KV FOR 11 HRS. 111 MM CELL



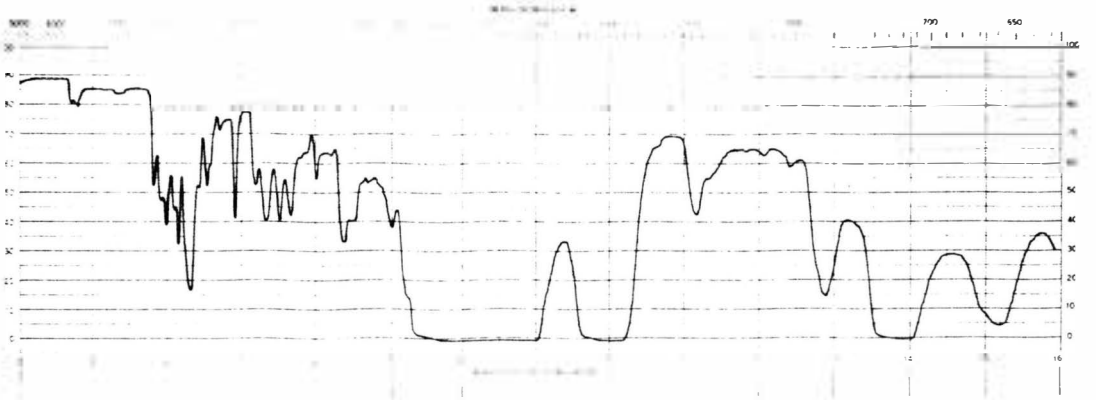
PURE DIMETHYL DISULFIDE BEFORE CORONA 111 MM CELL
0.5 ML LIQUID EVAPORATED TO 500 ML GAS



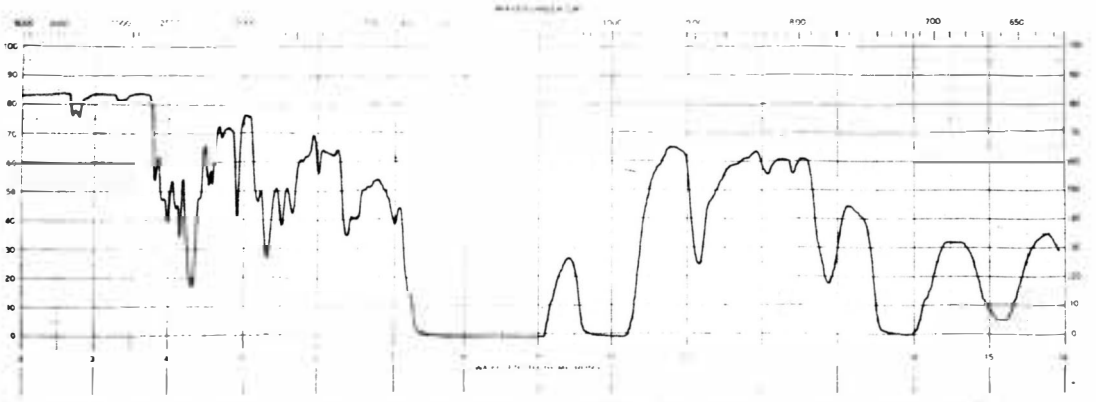
MOLAR RATIO 1 TO 10 18 KV FOR 3 HRS. 111 MM CELL

FIGURE 48. INFRARED OF DIMETHYL DISULFIDE AND PERFLUOROPROPANE

MOLAR RATIO 1 TO 20 11 KV 8 HRS. 45 MIN. 112 MM CELL



MOLAR RATIO 1 TO 40 15 KV 3 HRS. 55 MIN 111 MM CELL



MOLAR RATIO 1 TO 60 18 KV 3 HRS. 15 MIN. 112 MM CELL

FIGURE 49. INFRARED OF DIMETHYL DISULFIDE AND PERFLUOROPROPANE

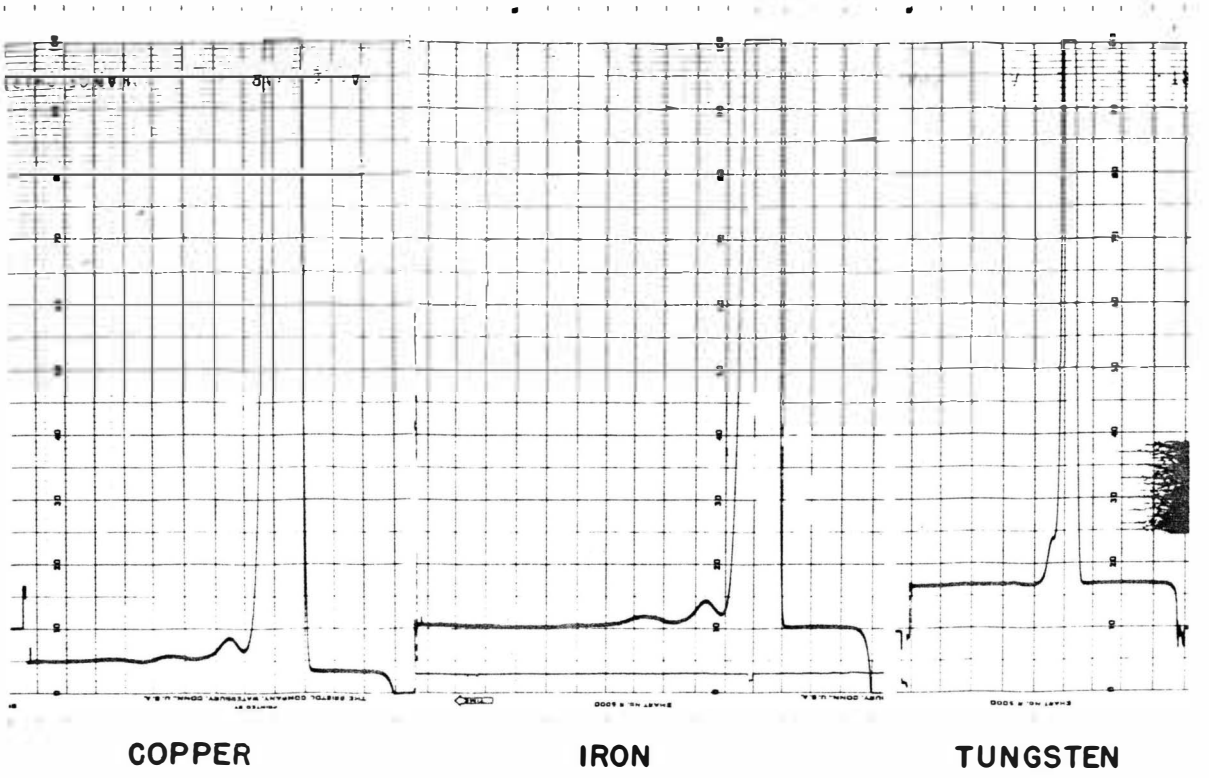
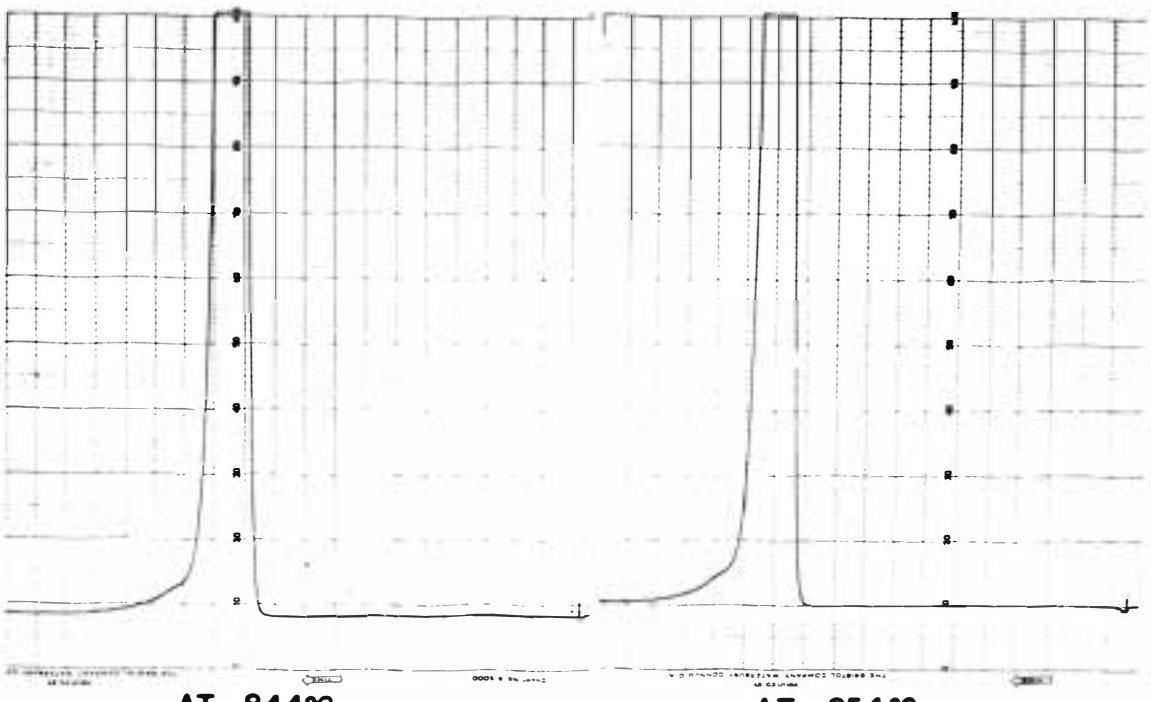


FIGURE 50. GAS CHROMATOGRAM OF PERFLUORO-PROPANE EXPOSED TO ARC DISCHARGE USING COPPER, IRON AND TUNGSTEN ELECTRODE

SAMPLE SIZE:	1	ML.
COLUMN LENGTH:	12	FT.
FLOW RATE:	15	ML/MIN.



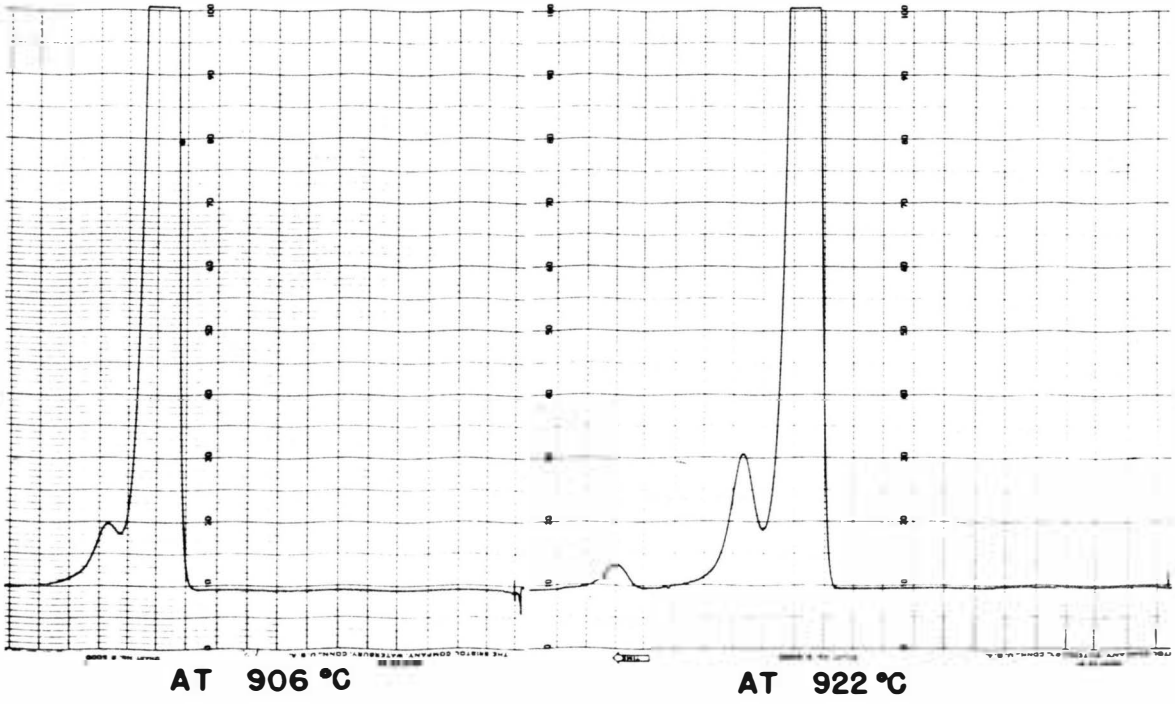


FIGURE 51. GAS CHROMATOGRAM OF PERFLUOROPROPANE EXPOSED TO THERMAL EFFECT AT TEMPERATURE 844°C, 854°C, 906°C, 922°C

SAMPLE SIZE:	5	ML.
COLUMN LENGTH:	25	FT.
FLOW RATE:	12	ML/MIN.

DISCUSSION

It is of interest to consider the possible causes for the observation (8) that there is an enhancement in dielectric strength of perfluorocarbon gases when diluted with nitrogen, a gas with a lower dielectric strength. If this effect were caused by the nitrogen acting as an inert diluent, then any inert gas should give the same effect at the same molar concentrations. None of the additives used in this present study seemed to qualify as an inert diluent since all gave differing effects on the extent of corona. Concentration optimums seemed to be dependent on the chemical nature of the diluent. Products differed. In some cases carbon and tars were formed. In other cases no visible solid residue was formed. Since pure perfluoropropane on exposure to corona deposits carbon on the electrodes, these gross observations indicated a considerable difference in product formation. Most conclusively, definite infrared evidence was obtained that the additives are consumed in the course of exposure to corona discharges. Since several of the additives used, notably ethyl methyl sulfide, thiophene, dimethyl disulfide and isopropyl mercaptan improved the initial corona properties over that for the pure perfluoropropane, there must be a mechanism whereby an additive can act as an inhibitor or as a scavenging agent for certain of the metastable intermediates thus inhibiting the chain reaction which leads to streamer formation. Whether nitrogen was acting as an inert additive or whether it too was behaving like the sulfur containing additives used in this study is not clear. Further

studies are needed in order to clarify this point.

Of the compounds selected for study, nitrobenzene was chosen for its known behavior as a free radical chain inhibitor and also for its aromatic ring which might act as an electron sink. The sulfur compounds were chosen because the mercaptans are efficient radical chain transfer agents and because thiophene was reported to form sulfur hexafluoride, perfluoromethane, perfluoroethane, perfluoropropane and perfluorobutane on reaction with fluorine (36). Since the production of elemental fluorine was suspected on the basis of liberation of iodine from an iodide solution by perfluoropropane gas exposed to an arc discharge, these sulfur compounds might reasonably be expected not only to pick up undesirable breakdown products such as fluorine but also to form gases with high dielectric strength in the process.

The product analysis was rendered difficult by a lack of known compounds with which the instruments could be calibrated. This was especially true for all the gas chromatography analyses. A number of these compounds are known, but the industries doing research with these compounds have been singularly reluctant to send samples. The synthetic approach has not yet been undertaken because elemental fluorine is involved with all of the consequent difficulties in manipulation.

The infrared analysis of the gases after exposure to corona gave evidence of being one of the potentially most useful tools for studying the chemical changes brought about by corona conditions. It was noticed that in the analysis of the 1 to 10 molar ratio of thiophene to perfluoropropane and in the products obtained in the 1 to 30 molar

ratio of ethyl methyl sulfide to perfluoropropane for three hours or less, that a broad band appeared at 3100 to 3700 $cm.^{-1}$. This might be due to a hydrogen bonded HF in the gas phase. It has been postulated that a number of polymers up to $(HF)_5$ exist in the vapor (25). It is interesting that on longer exposure to corona in the ethyl methyl sulfide series, this broad peak disappears completely. It is a moot point whether the band, if due to HF, disappears because the HF formed reacts with the glass of the cell or whether it undergoes secondary corona reactions. A substantiating bit of evidence that this band might be due to HF was the observation that the salt windows of the infrared gas cells were badly etched by these gas mixtures.

There was a fairly rapid disappearance of the C-H bands at 2800 $cm.^{-1}$ - 3100 $cm.^{-1}$ for thiophene and the C-H band at 2850 $cm.^{-1}$ for ethyl methyl sulfide. The latter seemed to disappear in about 15 minutes. However, the corona was repressed long after the disappearance of the C-H bands. In the case of isopropyl mercaptan, the C-H band remained much longer than for thiophene and ethyl methyl sulfide. However, since the longest experiment carried out for this additive was in the order of three hours, the full extent of the difference was not ascertained. The evidence seems to be definite that there is no correlation between corona characteristics and the disappearance of the C-H absorption frequency.

For thiophene, ethyl methyl sulfide, isopropyl mercaptan and dimethyl disulfide, there was a common strong peak formed at 2300 $cm.^{-1}$. In the time studies done with a 1 to 30 molar ratio of ethyl methyl

sulfide to perfluoropropane this peak became fairly strong after three hours and increased only slightly to its maximum size after eleven hours. It may well be that this peak is due to the sulfur-fluorine bond. It should be fairly easy to test this postulate by looking at the infrared spectrum of sulfur hexafluoride. At the time this study was carried out, this compound was not available. The appearance of this peak at 2300 $cm.^{-1}$ and the corona characteristics were also not correlatable.

The gas chromatography analysis was not as promising as originally anticipated. Regardless of the additive or lack thereof, all perfluoropropane samples indicated the same kind of result. There was a large peak representing the perfluoropropane followed by several smaller peaks which were thought to be perfluoroethane, perfluoromethane, perfluoroethylene and the like. An interesting aspect was that the thermal decomposition of pure perfluoropropane showed the same results as the corona studies. Until some calibration curves are obtained with known compounds, it will be difficult to decide if there are difficulties in a lack of resolution of the instrument. Resolution was checked to the extent of a successful separation of the hydrocarbon components of natural gas. There is a suggestion on the basis of the gas chromatography results that many of the corona products might be due to thermal effects. This should be checked by studying the infrared spectrum of the thermal breakdown products of perfluoropropane.

The corona characteristics provided some interesting data. In the method of presentation of these data, the more nearly vertical the initial and final points, the better the corona characteristic.

The closer the points are to the left, the less the observable corona. It can be seen that there is a marked variation in optimum molar ratios of additives to perfluoropropane. For ethyl methyl sulfide this optimum ratio seemed to be 1 to 30, for thiophene 1 to 40, and 1 to 60. For thiophene and ethyl methyl sulfide there was a decrease in corona on exposing the gas mixture to electrical stress for a period of time. Of the others isopropyl mercaptan, dimethyl disulfide and carbon disulfide improved the corona characteristics initially over that of pure perfluoropropane, but in the course of exposure to corona the mixtures began to behave worse than pure perfluoropropane. Nitrobenzene as an additive was a failure from the start.

SUMMARY

Evidence was obtained that the stable decomposition products of perfluoropropane after exposure to electrical stress do not in themselves begin to tell the story of the chemical changes taking place during the exposure process. The gas chromatographic analysis indicates much the same results for gas mixtures as well as for the pure gas. The number and variety of metastable species formed during the application of the electrical stress, however, varies considerably if we are to believe that the so-called corona measurement is a measure of these species. The corona values varied widely depending on amount and kind of additives mixed with the perfluoropropane. Some of the results indicated formation of free fluorine. The variety as well as lack of solid products formed indicated that removal or modification of the metastable intermediates can be accomplished by means of additives. Ethyl methyl sulfide not only indicated the suppression of metastable intermediates, but also prevented the formation of noticeable amounts of solid or liquid decomposition products. Thiophene, although not as effective as ethyl methyl sulfide, was also a promising additive. Evidence was obtained for structural changes by infrared analysis. These changes, however, did not correlate with the corona characteristics. Ethyl methyl sulfide was found to be effective corona-wise long after the marked changes observed in the infrared took place. Although the data at present is inconclusive, it is believed that further work with additives will shed considerable light on the secondary gas processes taking place under electrical stress.

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